



This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

### Usage guidelines

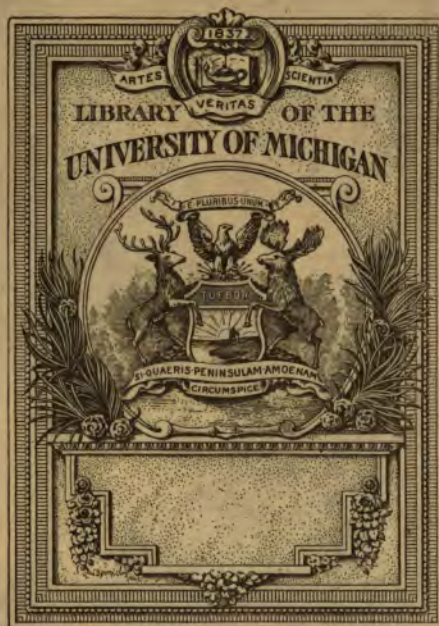
Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

- + *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
- + *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
- + *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
- + *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

### About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at <http://books.google.com/>



QD  
101  
11217



**A COLLEGE TEXT-BOOK**  
**ON**  
**QUANTITATIVE ANALYSIS**

**BY**  
**HERBERT RAYMOND MOODY, S.B. (M.I.T.), A.M.,**  
**PH.D. (COLUMBIA)**

**ASSOCIATE PROFESSOR OF ANALYTICAL AND APPLIED CHEMISTRY**  
**COLLEGE OF THE CITY OF NEW YORK**

**New York**  
**THE MACMILLAN COMPANY**

**1912**

*All rights reserved*

COPYRIGHT, 1912,  
BY THE MACMILLAN COMPANY.

---

Set up and electrotyped. Published September, 1912.

Stanbope Press  
F. H. GILSON COMPANY  
BOSTON, U.S.A.

33613-58  
Revised 3-9-26 NHP

---

ACKNOWLEDGEMENT

IS MADE

TO MY WIFE

EDNA WADSWORTH MOODY (M. I. T., 1893)

WITH WHOSE EFFICIENT COLLABORATION

THIS BOOK HAS BEEN WRITTEN.

---

I AM INDEBTED TO

PROFESSOR LEO FRANK GUTTMANN, PH.D., F.I.C., F.C.S.,

OF QUEEN'S UNIVERSITY, KINGSTON, ONTARIO,

FROM WHOM I RECEIVED HELPFUL SUGGESTIONS

WHEN ORIGINALLY LAYING DOWN THIS COURSE,

FOR CRITICISMS AND PROOF READING.

---





## FOREWORD

---

THIS book is issued with no thought of enriching the literature of Quantitative Analysis. The field has been covered so often and the number of typical analyses suitable for elementary classes is so limited that no great departure from regulation courses is possible.

The aim in view has been to prepare directions which shall be explicit, clear, adapted to those to whom quantitative analysis with its refinements is an unknown field and above all *to make obvious the unnecessary pitfalls that consume time*. For the last reason the author has placed the explanatory facts in large type on the same page and directly under the directions for procedure to which they relate. While this book has been in use in manuscript form during the last five years at the College of the City of New York this has been effective in two hoped for results: (1) The prevention of mistakes that are so often made before the student has turned to the end to read the explanations and warnings in the notes and (2) a clearer understanding of the reactions and changes at each step of the work.

Another object in view has been to make a book that will be useful to the student who is either taking up quantitative work by himself or with an instructor whose classes are too large to admit of much individual attention. This is more often the case than not. It is the writer's experience that for lack of specific directions the student, while the instructor is otherwise engaged, makes the fatal error which necessitates the repetition of perhaps hours of

work. There are accepted methods of manipulation, the result of tried experience, that insure correct analyses. The student cannot be expected to know these intuitively. Too much independence of action at this stage inevitably leads to a loss of time and to the acquiring of disadvantageous habits of manipulation. By the use of these minute directions he at once gets into the habit of correct manipulation, accomplishes more in the same time and, *for a beginner, gets unusually good results.*

There is much possible latitude in the choice of detail of methods in the analyses selected, but standard methods which have been found to serve satisfactorily with our own students are those used.

Only such facts and theories as are necessary to the full understanding of the development of the subject are included. For further details the student is referred to his instructor's lectures and to larger textbooks.

The author will gladly confer with instructors in other colleges concerning his system of "unknowns." The substances used for analyses are strictly unknown to the student who is consequently forced to rely upon his own work. A qualitative analysis gives no hint as to which sample has been given to him.

HERBERT RAYMOND MOODY.

COLLEGE OF THE CITY OF NEW YORK.

# QUANTITATIVE ANALYSIS

---

QUANTITATIVE ANALYSIS determines the amount of one or more of the constituents of a substance. The methods used in Quantitative Analysis may be considered as refinements of those already used in Qualitative Analysis.\* When it is merely a question of determining *what* elements are present in the substance to be analyzed, these less precise processes of Qualitative Analysis are adequate; when it is a question, however, as in Quantitative Analysis, of determining *how much* of one or more elements is present, the reactions selected for the process must produce more complete separation. To isolate completely one substance from one or more elements, requires definite, standard conditions fulfilled with the most scrupulous care, neatness and accuracy. To illustrate:

If ammonium oxalate be added to a mixture of magnesium and calcium chlorids to determine the per cent. of calcium present, difficulties are met by adding too much oxalate, and on the other hand by adding too little. In Qualitative Analysis, an indefinite amount of the ammonium oxalate added to the mixture of magnesium and calcium chlorids will precipitate most of the calcium as calcium oxalate and leave most of the magnesium in the filtrate. The *presence* of calcium is shown, which is all that is required. In Quantitative Analysis, there are two facts that must be taken into consideration. First, if only enough oxalate is added to throw

\* References are given in the text to the preliminary experiments in "Chemistry of the Metals" which apply in this later course.

out the calcium as calcium oxalate, some of the calcium oxalate will dissolve in the magnesium chlorid and make the per cent. of calcium too low. Second, if enough ammonium oxalate is added to convert both the calcium and magnesium to oxalates, then the calcium oxalate will drag down with it some of the magnesium oxalate and make the per cent. of calcium too high. Hence the analyst is between two dangers: (a) he may lose some of the calcium because of the solubility of the oxalate in magnesium chlorid or (b) he may add to the precipitate through contamination.

Later, when analyzing for calcium and magnesium, the student will be given precautions which reduce these dangers to a minimum. *Absolute adherence to directions as to quantities, time and manipulation is necessary if the student is to get accurate results.*

*A Quantitative Analysis* may be made by Gravimetric or Volumetric methods:

In *Gravimetric Analysis*, which includes electrolytic work, measurement by weight is the important factor; in *Volumetric Analysis*, measurement by volumes. *Electrolytic Analysis* involves the isolation of an element by use of the electric current.

## SECTION I

---

### **GRAVIMETRIC ANALYSIS**



## GRAVIMETRIC ANALYSIS

---

### Apparatus

THE student is already familiar with most of the apparatus used in gravimetric analysis, such as beakers, evaporating dishes, flasks, lamps, stirring rods, filter papers and funnels.

The following details should, however, be noted:

(1) *Stirring rods* must be rounded with even more care than in qualitative work to avoid the possibilities of spoiling beakers by scratching. Precipitates adhere to such scratches and are removed from them with difficulty. For the complete removal of precipitates, stirring rods should have at one end about one inch of black rubber tubing, fitted closely to the rod and just covering the end. This rubber end should not be kept standing in a solution, especially while the solution is boiling. It should be reserved for the latter part of the filtration when the last of the precipitate is being removed from the beaker. Such a stirring rod is known as a "policeman."

(2) Ordinary *filter paper*, the sort used in Qualitative Analysis, is not suitable for the final filtration of quantitative precipitates. Such paper is used only in preliminary filtrations, to cover the funnel when it is placed in the drying oven and to place on the filter-stand under beakers during the period of filtration. For the

final filtration a special "washed" filter-paper is used. Any of the various grades are suitable. The Schleicher and Schüll, No. 589, 11 cm. in diameter, is a convenient size and a satisfactory quality. Each paper has a uniform ash of 0.00017 grams. Allowance in the final weighing may therefore be made and this weight of ash deducted from the total weight of the substance in the crucible. Such papers are expensive and should be used only for final filtrations. It is advisable to keep filter papers in envelopes or boxes to prevent them from collecting dust or other ponderable matter.

(3) *Funnels* for this work should be of the so-called Bohemian-glass type, with sides at an exact angle of  $60^\circ$  and with a long stem which is ground to a point. A funnel of this shape filters much more quickly than one of the ordinary kind (see fact 7, page 36).

In addition to the above apparatus, use will be made of: (4) weighing tubes; (5) wash bottles; (6) casseroles; (7) filter flasks; (8) steam baths; (9) air baths; (10) crucibles; (11) triangles; (12) desiccators and (13) the analytical balance.

(4) *Weighing tubes* may be of the ground-glass-stopper type with either a flat or round bottom or a  $2\frac{3}{4}$ -inch by  $\frac{1}{2}$ -inch test tube fitted with a good grade of cork stopper. The latter is equally desirable.

(5) *Wash bottles* used in Quantitative Analysis should have tips small enough to emit a sufficiently fine stream of water to avoid spattering precipitates when the stream strikes them. For the convenient handling of a wash bottle containing hot water, the neck should either be wound with cord, covered with cork sheets or supplied with some other similar device.

(6) *Casseroles* are more often used than evaporating dishes, altho they serve the same purpose. It is, of course, fatal to an



analysis to lose even a minute amount of the solution. The handle on the casserole makes it much easier to avoid spilling and is more convenient to hold while filtering.

(7) *Filter flasks*, or suction bottles, facilitate the filtering of gelatinous and other precipitates. The funnel stem is inserted in a one-hole rubber stopper fitted to the neck and the side-neck is attached to the vacuum outlet by rubber "pressure" tubing. The tip of the stem of the funnel should come well below the side neck. In order to avoid the possibility of the introduction of liquids or corrosive vapors into the vacuum pipes and apparatus, a gas wash bottle must be interposed between the filter bottle and the vacuum cock on the desk. To avoid breaking the tip of the wet filter paper by the increased pressure on it, the apex of the funnel should contain either a perforated platinum cone or a small cone made by folding a "hardened" filter paper, "S. & S." No. 575, 7 cm. in diameter.

(8) *Steam Baths* are used for evaporations which are rarely made over the free flame because of the possibility of loss through too violent ebullition. If the Bunsen lamp is used, the beaker or casserole should stand either on a sand bath (a shallow iron tray containing a quarter of an inch of sand) or on an iron plate covered with a sheet of asbestos board.

(9) *Air Baths* are used for drying precipitates in funnels and for determining water of crystallization, hygroscopic moisture, etc. They may be simple copper ovens with shelves, heated by a lamp, or they may be larger and heated either with a steam jacket or steam pipes in the base.

(10) *Crucibles* for all ordinary ignition of precipitates may be of Berlin porcelain in spite of the fact that some precipitates are not so easily brought to a constant weight in porcelain as in platinum crucibles. Such porcelain crucibles should be heated with great

care to avoid breaking. However, unless expense prohibits their use, platinum crucibles are far more desirable except in the case of precipitates which are easily reduced; as, for example, those obtained in lead and phosphorus determinations. In such cases the reduced metal will alloy with the platinum and spoil the crucible. For work of this kind porcelain crucibles always should be used.

Two important facts should at this point be learned:

(1) *Platinum alloys with certain metals.* A student sometimes forgets this until he has ruined his expensive platinum crucible.

(2) Before selecting the sort of crucible for use, the chemical change that is to take place in the precipitate which is being ignited should be considered.

Platinum containers should be used for most fusions and always for the treatment of substances with hydrofluoric acid.

Whichever crucible is employed, it must first be ignited and cooled in the desiccator before weighing. Otherwise, when it is ignited with the precipitate, the crucible itself might change in weight.

Crucible covers are always weighed with the crucible, as ignited precipitates should be weighed covered in order to avoid absorption of hygroscopic moisture. Covers, by keeping out the air currents, also prevent the loss of finely divided precipitates during ignition.

Crucibles must be cleaned after each analysis. Porcelain crucibles may be cleaned by using any solvent of the adhering substance which does not react with porcelain.

If platinum crucibles are used, the student should observe the following rules and precautions issued by J. Bishop & Co., Malvern, Pennsylvania.

#### CARE AND USE OF PLATINUM WARE\*

To insure long and satisfactory service, platinum ware should be perfectly clean and bright before each operation in which it is employed, and to that end it is advisable to carefully clean, dry and polish it immediately after it is used.

\* Courtesy of J. Bishop & Co. Platinum Works, Malvern, Pa.

The cleaning may be accomplished by boiling in dilute hydrochloric acid or by immersing in fused potassium bisulphate for a few minutes and removing the salt by means of boiling water.

By rubbing the surfaces with moist talc or fine sea sand (free from sharp or angular grains) the platinum may be freed from adhering substances and polished without injury or appreciable loss of metal.

After polishing, the platinum should be thoroughly rinsed in distilled water and finally ignited.

#### PRECAUTIONS TO BE OBSERVED

In making ignitions or fusions in platinum vessels by means of the Bunsen burner, the upper non-luminous cone only should be employed, and not the inner cone, nor should a smoky flame be used, as the action of a flame containing free carbon will result in the formation of a carbide of platinum, causing the metal to become brittle.

Fusions in which hydrates of sodium, potassium, barium or lithium are used should not be performed in platinum vessels, as they attack the platinum at high temperatures. Great care should be observed in igniting phosphates in platinum crucibles, as the presence of reducing substances, such as the charcoal of the burnt filters, may cause the reduction of small quantities of phosphorus, which, combining with the platinum, render it quite brittle.

Compounds of silver, lead, tin, bismuth, arsenic and antimony should not be ignited in platinum vessels as the reduction of metals having low melting points may result in the formation of alloys with the platinum.

Evaporations and fusions in which chlorine, iodine or bromine are set free should not be performed in vessels of platinum.

(11) *Triangles.* During the process of heating, crucibles are placed upon triangles of such a diameter as to admit of the crucible resting vertically or on its side at an angle of forty-five degrees.

For all ordinary purposes "pipe-stem" triangles answer, but those made of heavy platinum wire (gage 18, or heavier) are in some respects better. These latter need not be made entirely of platinum, but a triangle of platinum wire may be stretched from copper loops at the center of the sides of a larger copper wire triangle (gage 12, or over). The triangle must be kept scrupulously clean. If it has not been well cleaned, after a carelessly regulated fusion, for instance, adhering matter may attach itself to the next crucible heated upon it and increase its weight.

(12) *Desiccators*, as the name indicates, furnish an inclosed space in which the air is perfectly dry and from which, therefore, no moisture can be deposited on crucibles or precipitates to add to their weight as they cool. There are various types of desiccators, a most convenient form of which will be found in the five-inch Scheibler which is fitted with a three-hole porcelain crucible plate and filled in the lower chamber with a few sticks of solid potassium hydroxid.\* The ground-glass undersurface of the rim of the cover should be *lightly* covered with vaseline or with a mixture of equal parts of beeswax and paraffin melted together.

(13) The *Analytical Balance* is sufficiently sensitive to weigh to one ten-thousandth part of one gram. The pillar, beam and the pans are its three most essential parts. The pillar is surmounted by the beam, the halves of which are termed the "arms," two equal divisions of a lever. The beam is supported on a fulcrum at the top of the pillar. The arms are capable of adjustment in length by means of a micrometer screw at the ends. Two equal loads on the two pans, therefore, produce equilibrium or equal oscillations on either side of the center. The right-hand arm is divided into five or ten equal parts, each in turn subdivided into ten equal parts. A two-legged piece of platinum wire, called a "rider," may be set down upon this arm at any point by means of the rider hook, which is moved by the rider rod projecting outside of the case at the top of the right-hand side. When placed upon a whole division, the rider is equivalent to a corresponding number

\* Fused anhydrous calcium chlorid can be used if preferred.

of milligrams. The fractions of divisions, consequently, read tenths of milligrams. For accurate results the balance should be level on the table. It may be made so by adjusting the height of the two front legs of the case until the spirit level or plumb bob at the base of the pillar indicates proper adjustment.\* Friction in the balance at the point of support must as far as possible be avoided. This is accomplished by using "knife-edges" to give as little supporting surface as possible and by making all supporting surfaces of hard metal. The "knife-edges" are of hard steel resting upon agate.†

### THE WEIGHTS

It is rarely necessary in gravimetric work to weigh anything heavier than one hundred grams. A box of weights, therefore, usually contains weights of the following denominations:

50 grams	20 grams	10 grams	10 grams
5 "	2 "	1 gram	1 gram
0.5 gram	0.2 gram	0.1 "	0.1 "
0.05 "	0.02 "	0.01 "	0.01 "

a total of 99.99 grams.

It is evident that if the weights oxidize or corrode, their value would change. They must therefore be protected from dirt and fumes and must be handled only with forceps. They should never be left out of the box, which should always be kept tightly covered. Pure platinum or gold would be the most permanent materials for weights but for ordinary work their value prohibits their use. The large weights are of brass, tin, etc., and may be platinum or gold plated. Fractional weights are usually of pure platinum.

\* Such adjustments should be made by the instructor and not by the beginner, whose inexperience is likely to result in making a bad matter worse.

† For details of construction and theory of the balance, the student is referred to Clowes and Coleman's "Quantitative Analysis," pages 1-14; Morse's "Quantitative Chemistry," pages 1-30; Fresenius's "Quantitative Analysis," pages 1-26; Olsen's "Quantitative Analysis," pages 7-20; and Treadwell's "Analytical Chemistry," Vol. II, pages 6-16.

**GRAVIMETRIC ANALYSIS** is the process of determining the relative amount of a constituent of a substance by:

(I) Weighing a definite quantity of the substance to be analyzed,

(II) Isolating the element or radical sought either as the element itself or as a definite, insoluble, pure compound,

(III) Freeing this element or compound from admixed liquids or solids by filtering and washing,

(IV) Igniting to a stable compound of known composition,

(V) Weighing the element or stable compound, and

(VI) Calculating the per cent. from data obtained.

## PROCESSES EMPLOYED IN GRAVIMETRIC ANALYSIS

## I. Weighing

The weight of a substance taken for analysis varies. An ordinary charge runs from 0.2 grain to 1 gram, but, under some conditions, 5 or even 10 grams might be required. Within certain limits the larger the amount taken for analysis the more accurate the result, but no amount should be large enough to give an over bulky precipitate. An analyst in his selection is guided by the quantity of the unknown compound at hand and also by the relative amount of the element sought in the substance. If it contains a large amount of the element sought, a smaller weight of the substance is taken than if it contains, for example, only a fraction of a per cent.

## A. Precautions

- (1) Always use the same balance.
- (2) Sit directly in front of the balance to avoid parallax.
- (3) Borrow neither weights nor riders from another balance.
- (4) *Allow the knife-edges to rest upon the agate bearings only when the pans are swinging.* At all other times the cradle should be raised by the knob or wheel in front. Form the habit of immediately raising the cradle the moment equilibrium has been established.
- (5) Never remove weights from the pan nor put them upon it unless the beam has been arrested by raising the cradle.
- (6) Never weigh a substance upon the balance pan, but have it in a crucible, weighing tube or on a tared watch glass.
- (7) Never put a hot nor a wet dish on the balance pan for it may both hurt the surface of the pan and change the weight. A hot dish produces ascending air currents and therefore weighs too little. A dish below the temperature of the balance produces descending currents and therefore weighs too much.

- (8) Keep the front door of the balance closed except during the time of putting on or taking off the weights or dishes. If the balance is provided with side doors, the front door need scarcely ever be opened. The final operation of the weighing with the "rider" should be done with the case entirely closed. If any door is open, air currents may cause an error.
- (9) Weigh all precipitates which are markedly hygroscopic, volatile or absorbers of carbon dioxide with the crucible cover on. The crucible and cover should therefore be weighed together at the beginning of the analysis.
- (10) Never handle the weights except with the forceps provided in the box.
- (11) The center of the pointer scale should be the zero point. Unless the balance is in perfect adjustment, this will not be the case.

Occasionally determine the zero point as follows:

Imagine the divisions on the pointer scale numbered from 0 to 20 from left to right. Make three readings on the left and two on the right, as, for example:

Left.	Right.	
2.50	17.00	$\frac{16.63 + 3.08}{2} = 9.8$
3.00	16.25	
3.75	2)33.25	that is, the zero point,
3)9.25	Mean, 16.63	9.8, is 0.2 of a space
Mean, 3.08		at the left of the middle division.

The position of the zero point changes because of varying temperature, defective condition of the knife-edges or from jarring.

#### B. Method of Weighing.

Unless special directions are given for weighing in a tared watch glass or crucible, the method of "direct weighing" of the charge is not to be used. The method of "indirect weighing," weighing by difference, is as follows:

The weighing tube is partially filled with the prepared substance stoppered, carefully wiped, weighed and the weight recorded. The approximate amount of salt is emptied from the tube into a beaker, the stopper replaced and a second weighing made. The



difference between the two weights is the weight of the charge. This process is given in detail under the "Determination of Aluminium."

The weight of the charge specified in the directions is only approximate. For example, if the directions call for 0.5 gram, a charge weighing 0.4895 gram or one weighing 0.5103 gram fulfills the conditions.

### C. Directions for Weighing

- (1) With tongs, take the article to be weighed and put it through the side door on the center of the left-hand pan.
- (2) If the article has never been weighed before,\* trials should be made, according to (3), to determine which one or combination of two or more of the larger weights comes the nearest to causing equilibrium. During such trials, *the cradle should be lowered but part way* and the pointer carefully watched in order to avoid the *violent* descent of either pan, which may put the balance out of adjustment.
- (3) With the forceps, put the large weight selected on the center of the right-hand pan. If the right-hand pan descends, the weight is too large and the next smaller denomination should be used. If this proves too light, add smaller weights till the total weight just falls short of balancing the article on the left pan and finish with the rider. For example: A twenty gram weight proves too heavy. Raise the cradle. Remove the twenty-gram weight. Put on a ten-gram weight. Partly lower the cradle carefully. This is too small. Raise the cradle. Try a combination of ten and five. Lower the cradle. This is not enough. Raise the cradle. Make a combination of ten, five and two. Lower the cradle. This is not enough. Raise the cradle. Add one gram. Lower the cradle. This causes the right-hand pan to descend. Raise the cradle and put the one-gram weight back into its place in the box. Proceed with the smaller fractional weights until the last one added just falls short of causing equilibrium. Close the door and determine the exact position of the rider necessary to produce equilibrium.

\* For the student's guidance, it may be stated that an average porcelain crucible and cover weighs about 16 grams, an average 15 c.c. platinum crucible and cover about 12 grams and a 2½ inch-platinum evaporating dish about 30 grams.

Experience teaches by observing the swing of the pointer, about how much too heavy or how much too light a given mass is and will help to determine the next combination.

After equilibrium has been established:

- (4) Raise the cradle.
- (5) Add up the weights on the pan and record in the notebook.  
This should be done in ink and at once. This rule is insisted upon.\*
- (6) Check this result by noting the empty spaces in the box.
- (7) Remove the weights with the forceps and put each in its proper place in the box.
- (8) Remove the crucible or other container.
- (9) Close the doors.
- (10) Lift the rider.
- (11) Call the Instructor's attention at once to anything that may have been spilled within the balance or to any part of the balance that may have become disarranged.

\* For the first two analyses, all recorded weights should be stamped "checked" by the Instructor before the weights are removed from the pan. This not only insures good work on the student's part but corrects errors due to inexperience.

## II. Isolating the Element or Radical Sought

### SOLUTION OF THE SUBSTANCE

Getting the original substance into solution is the first necessary step in the process leading up to precipitation. A water solution is usually preferable. If it cannot be dissolved in water it should be dissolved in acid. Here a knowledge of solubilities is essential. For instance, an alloy or compound containing lead should be dissolved in an acid like nitric acid. An unthinking analyst might try sulfuric acid, not recalling the fact that lead sulfate is insoluble and that therefore no solution could result. Many compounds and ores are wholly or in part insoluble in acids, cold or hot, or even in *aqua regia*. Such substances should first be made to undergo a preliminary fusion to change them to soluble compounds (see under "Determination of Silica," page 78). The principle underlying this method is as follows:

All carbonates and all sodium salts are decomposed by strong acids. When a compound is heated with sodium carbonate, at the temperature of fusion, the constituents are transposed in such a manner as to render them soluble, carbonates of the metals of the compound are formed and the acid radicals combine with the sodium. Since all carbonates and all sodium salts are decomposed by strong acids, the originally insoluble compounds have been changed into soluble forms. The reactions on page 78 show what happens upon the decomposition of a silicate which may be taken as a type of such a refractory substance.

### REAGENTS

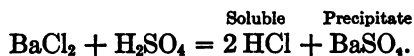
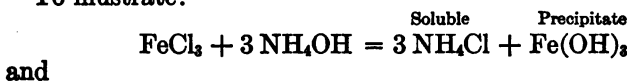
After getting the original substance into solution, the characteristics of reagents selected to cause precipitation should be considered.

A reagent is used which gives a definite and completely insoluble compound with the element to be determined. For instance,

sulfuric acid could not be employed to determine calcium altho it gives a precipitate of calcium sulfate in a fairly strong solution. Calcium sulfate is somewhat soluble and consequently an oxalate which gives a completely insoluble compound is always used.

Reagents most often employed are acids, their sodium or ammonium salts, or alkalies. As they are readily soluble this makes easy the preparation of their solutions for reagents. As a soluble salt or acid results from the metathetical reaction with the compound containing the element to be precipitated, most of it passes into the filtrate and what is left may easily be washed from the precipitate.

To illustrate:



Other compounds than the soluble salts and acids used for precipitations must be intelligently selected with the foregoing facts in mind.

### PRECIPITATION

It is evident that to completely separate one element from one or more others in the same solution, a sufficient amount of a reagent must be added to precipitate in an insoluble form all of the given element, which may then be filtered off from the simultaneously occurring substances in the solution. It is not always possible to form a precipitate entirely free from other compounds. In such cases, subsequent purification is resorted to (see "Determinations of Calcium and of Silica" for two types of such procedure). When working with substances of known composition, as with alum in the first determination, it is easy to calculate the amount of reagent required. This is not often possible, since the composition of the substance and amount of each element present is unknown. Generally, therefore, the reagent, which should always be hot when conditions permit, is added slowly with constant stirring of the solution until no further precipitate forms. This point may be determined by letting the precipitate settle and noting whether a few more drops of the reagent produce any

precipitate in the clear, supernatant liquid. Filtrates always should be re-tested for complete precipitation.

To be properly done, in Quantitative Analysis, precipitation requires a good, clear knowledge of solubilities,—both the solubility of the substance in the liquid used and the solvent action of substances simultaneously formed should be considered (for example, see the precautions necessary for the precipitation of calcium in the presence of magnesium, pages 73 and 74).

A study of precipitation, then, the process of making insoluble compounds, involves knowledge of the facts underlying the phenomena of solution.

#### IMPORTANT FACTS ABOUT SOLUTIONS \*

1. Conditions being the same, a great variation is noticed in the solubility of different solids in the same liquid.

2. No solid is absolutely insoluble. Even barium sulfate dissolves to the extent of 1 part in 400,000 parts of water.

3. Heat generally aids solution. A few exceptions to this rule are noted. Calcium citrate is more soluble in cold water than in hot water. Sodium chlorid, however, is about as soluble in cold as in hot water. Heat is an aid to the solution of metals and minerals in acids.

4. Water is the most universal solvent and has some solvent action on almost everything. As previously stated, a solvent must be selected to suit the individual case. No general rule can be given. It should be remembered that the use of a *concentrated* acid often *appears* to fail to give solution because the compounds formed are not soluble in *strong* acid. Later dilution will often cause complete solution. Even with a somewhat soluble compound, a saturated solution may result and more water be needed to destroy the saturated condition.

5. Dissolved substances tend to distribute themselves evenly throughout the solvent but the process is slow and should be aided by stirring or shaking. This is particularly to be observed in making standard solutions.

\* See "McPherson and Henderson" and other larger works for elaboration of some of these facts.

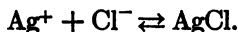
6. All substances whose solutions conduct the electric current *dissociate* when they dissolve in water. That is, the molecule splits into two or more parts called *ions* which are as free to move about in the solution as are independent molecules. These ions carry electrical charges and hence differ in their properties from the atoms or molecules. (See under "Ionization," page 85.)

7. The equilibrium between substances in solution may be disturbed and a reversible reaction may go to completion in three ways:

- (a) A gas may form and escape from the solution.
- (b) An insoluble solid may form.
- (c) Two different ions may form undissociated molecules.

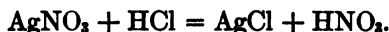
8. Section (b) in the foregoing paragraph governs the phenomena of *precipitation* as follows:

If  $\text{HCl}$  and  $\text{AgNO}_3$  are brought together in solution the following ions will be present  $\text{H}^+$ ,  $\text{Cl}^-$ ,  $\text{Ag}^+$ ,  $\text{NO}_3^-$ . The ions  $\text{Ag}^+$  and  $\text{Cl}^-$  will then set up the equilibrium



Silver chlorid is almost completely insoluble in water and the formation of very little of it causes a supersaturated solution and the excess of the salt precipitates. More ions of silver and chlorine then unite until all have been removed from solution.

The following reaction is then complete:



The table on page 21 will give the student a knowledge of solubilities of common compounds.

## SOLUBILITIES OF METALLIC SALTS\*

S, soluble in water. s, sparingly soluble in water. i, insoluble in water, but made soluble by acids. I, insoluble in water or acids. al, sparingly soluble in water, not transposed by acids. Si, soluble in acidulated water.

	Aluminium.	Ammonium.	Antimonious.	Barium.	Bismuth.	Cadmium.	Calcium.	Chromium.	Cobalt.	Copper.	Gold (triad).	Hydrogen.	Iron (dysd).	Iron (triad).	Lead.	Magnesium.	Manganese.	Mercuric.	Mercurous.	Nickel.	Potassium.	Silver.	Sodium.	Stannic.	Stannous.	Strontium.	Zinc.
Acetate.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Arsenate.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Arsenite.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Borate.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Bromide.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Carbonate.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Chlorate.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Chloride.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Chromate.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Cyanide.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Ferricyanide.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Ferrocyanide.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Fluoride.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Hydroxide.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Iodide.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Nitrate.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Oxalate.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Oxide.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Phosphate.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sulphate.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sulphide.....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..

\* Inserted here through the courtesy of the D. Van Nostrand Co., N.Y.

### III. Filtering and Washing

These are the two most tedious processes of Analytical Chemistry. Altho it is possible by suitable care to hasten them, they should not be slighted. They are facilitated by the use of well-made funnels, accurately fitted filter papers and, in some cases, by the use of suction. At best, however, they are both time consuming and whenever possible should be carried on simultaneously with other work.

As small a filter paper as the amount of precipitate will allow should be used. To wash a small amount of precipitate spread out over the paper requires an unnecessarily large amount of water, which should be avoided. The paper should not extend above the edge of the funnel and should preferably come only within one-fourth of an inch of its top edge.

It is desirable to carry on as many filtrations as possible at the same time. A number of these will not require much more time than a few. Filtration should be started as soon as possible after the beginning of the laboratory period in order that it may be finished at the end. It should be kept in mind that washing cannot be finished if the precipitate has been allowed to stand any length of time in an incompletely washed state. This is particularly true of gelatinous precipitates such as the hydroxids of aluminium and iron, which dry rather quickly and form a non-porous, film-like mass. Such dried precipitates inclose permanently any soluble salts which might have been left in them. Unless such salts happen to be volatile they still remain after the ignition of the precipitate, whose weight they increase and cause a consequent error in the result. It is evident that it is just as fatal to accurate results to leave in the mass of the precipitate any substance which should be washed away as to fail to obtain all of the element sought.

The precipitate, then, should be perfectly washed and, in order to prove that it is washed, the last few drops of the filtrate



should be tested for some ingredient known to have been present. Strangely enough this step is often ignored by beginners. Any constituent known to have been in the filtrate may be the one tested for. If an acid or alkaline solution is being filtered it is customary to use the simple litmus paper test. This is not only a delicate test but is also advantageous in that the litmus paper can be washed off and the loss of the tested drop avoided.

If the filtrate is to be used for the analysis of some other substance, only the fewest possible number of drops should be used when testing for complete washing. Such tests should not be made until it is fairly certain that the washing is complete so that the loss of any considerable quantity of the substance in the filtrate may be avoided. In other words, the filtrate should not be used for testing for complete washing until it is probable that the liquid is wash water only or an extremely dilute solution.

#### WASH WATERS

It is important that no more wash water be used than is absolutely necessary to remove that which does not belong to the precipitate. When the filtration is sufficiently advanced, the filtrate should be frequently tested both to save time and to avoid unnecessary washing. Too much washing (1) wastes time, (2) needlessly increases the volume of the filtrate and (3) as no substance is entirely insoluble if treated with a sufficient volume of water, tends to dissolve some of the precipitate.

Repeated treatments with small amounts of wash water give better results than the addition of all the water at once; that is, in washing a precipitate it is more advantageous to wash "by decantation" ten times with a little of the wash water each time than to wash once only with the total amount used in the successive volumes.

Hot water ordinarily is better than cold. It runs through the filter more quickly and is more efficacious in removing the substance to be washed out.

In order either to avoid the dissolving of some substance in water or to increase the solubility of the substance to be removed, special wash waters are often used. These are commonly dilute

acids, sometimes dilute alkali and, occasionally, such mixtures as alcohol, ammonia and water or acidified solutions of salts such as ammonium nitrate.

### EVAPORATION OF LIQUIDS

Filtrates, owing to the volume of wash water used, are often much too dilute. For this and for other reasons, such as the necessity of boiling out an excess of volatile alkali or acid, it is often necessary to boil down liquids which later are to be treated quantitatively. It is obvious that any liquid which spatters out removes with it a certain amount of the solids in solution, a loss that later causes a lowering of the per cent. of the substance determined. Too rapid boiling is therefore inadvisable.

If simply the evaporation of the water in the filtrate is the object, the beaker should be covered with a watch glass (sitting upon a glass triangle) and should be allowed to evaporate slowly at a temperature just below that of ebullition. If a solid is suspended in the liquid to be evaporated, still greater care should be exercised. Steam forms in the mass of the solid and, upon expanding, forces it violently upwards, giving rise to what is known as "bumping," which is very likely to cause a loss.

Evaporations, if done directly above the lamp, should be carried on over a moderate flame. Preferably they should be done on a gas or electric hot plate covered with a thin sheet of asbestos. Still better would be the use of a steam hot plate or steam bath upon which there is no possibility of ebullition and spattering and which may be left running all night without danger of fire.

#### IV. Ignition to a Stable Compound

*Ignition* in Analytical Chemistry is the process of heating a substance without allowing the direct access of the flame to the compound heated. It is accomplished by at first heating the crucible only hot enough to destroy the filter paper by dry distillation and later by increasing the heat. If the precipitate is to be subjected to the high temperature of the blast lamp, it will be mentioned in the directions.

Hastening the process of ignition, which is a temptation, is unwise, as it is almost sure to make the result too low.

Ignition may or will be the cause of any or all of the following changes:

(1) Water of composition or water mechanically held may be evolved.

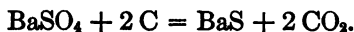
(2) The filter paper will distill.

(3) The carbon of the filter paper will oxidize.

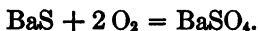
(4) The composition of the precipitate may undergo a chemical change, as:



(5) The precipitate may be reduced as:



(6) The precipitate may be oxidized as:



A precipitate may or may not be changed upon ignition; if changed, it must change completely to a definite new compound. If an incomplete or indefinite reaction would take place during the burning off of the filter paper or if something would be lost by volatilization, ignition should be omitted and the precipitate weighed upon a "tared" filter paper or upon an asbestos layer ("felt") previously weighed in a Gooch crucible. In either of these latter cases, the precipitate on the paper or asbestos should be completely dried in an air bath and weighed without ignition.

### V. Weighing the Element or Stable Compound

Repeated ignition, cooling and weighing eventually give two nearly the same consecutive weights, called "constant weights." Two or more consecutive weights do not constitute a constant weight if there is a greater variation than three-tenths of a milligram, 0.0003 gram. The completion of the process of igniting to a stable compound is shown only when a constant weight has been reached.

If a precipitate is hygroscopic, it is necessary to hurry the weighing that the water absorbed may not add to its weight. Before the crucible is taken from the desiccator the larger units of the weight of the crucible may be placed on the pan. Upon reweighing, all of the weights in the box used in the previous weighing may be first put into place and the weighing finished with the rider.

## VI. Calculating the Per Cent. from Data Obtained

Sample calculations are given at the end of each new method if there is any new principle involved. These serve only as a basis upon which to work. Facility in calculation may be acquired by an exhaustive variety of problems assigned by the Instructor or taken from the following books:

Baskerville and Estabrook's "Chemical Problems."

Well's "Textbook of Chemical Arithmetic."

Hale's "Calculations of Chemistry."

Lupton's "Chemical Arithmetic."

The initial substance is weighed only to the fourth decimal place, as, for example, 0.2343 gram. It is therefore futile in the various steps of the calculation to use figures beyond the fourth decimal place. In subtracting the ash, for instance, use the figures as follows:

$$\begin{array}{rcl}
 \text{precipitate} + \text{ash} = 0.1389 & \text{or} & \text{ppt.} + \text{ash} = 0.1389 \\
 \text{ash} = 0.00007 & & \text{ash} = 0.00014 \\
 \text{precipitate} & = 0.13883, \text{ use } 0.1388 & \text{ppt.} = 0.13876, \text{ use } 0.1388.
 \end{array}$$

In calculating the results of analyses the use of logarithms is to be preferred, not only because it saves time but also because of the fewer figures employed there is much less possibility of error.

## FACTORS

The element or compound isolated is not always weighed in the form in which it is to be reported, as, for example, iron may be weighed as ferric oxid,  $\text{Fe}_2\text{O}_3$ , and reported as per cent. of iron. The relationship between the molecular weight of the element or compound sought and the molecular weight of the element or compound reported is expressed by a *factor* found by making a proportion between the two. The factor used to change barium

sulfate,  $\text{BaSO}_4$ , into terms of barium oxid,  $\text{BaO}$ , for instance, may be found as follows:

$$\text{BaSO}_4 : \text{BaO} = \text{Weight of the BaSO}_4 : x.$$

$$x = \frac{\text{BaO}}{\text{BaSO}_4} \times \text{Weight of BaSO}_4.$$

$$\frac{\text{Molecular weight of BaO}}{\text{Molecular weight of BaSO}_4} = \frac{153.4}{233.5} = 0.6571 \text{ factor.}$$

Therefore, weight  $\text{BaO}$ , or  $x = 0.6571 \times \text{weight of the BaSO}_4$ .

A table containing all the factors and their logarithms needed in calculating the results of the analyses in this course may be found on page 155.

## PLANNING THE WORK, ETC.

The student should particularly note that the one who accomplishes the most analytical work is he who plans in advance and who carries on several processes at once. He reads ahead in the directions and sees the place at which a wait is to occur, — an evaporation, a dehydration, etc., — and makes sure that there is some other work sufficiently advanced to at once occupy the time.

It is necessary to state that absolute cleanliness, nothing less, must be observed. It will be mere luck if even fair results are obtained under other conditions. A linen towel should be used for the final wiping of all porcelain and glass ware. The free use of labels bearing explicit statements is necessary if one is to avoid error. Whenever possible, dishes should be covered with watch glasses.

### NOTEBOOKS

Careless records of results are almost certain to bring disaster. To eliminate this source of trouble, a notebook is a necessity.

The following directions are to be observed:

- (1) Use the left-hand page for a résumé of the process and for keeping a complete record of anything unusual that happens throughout the entire analysis.
- (2) Record weights always in ink directly into the book. Never use loose bits of paper.
- (3) On the first two analyses have each weight stamped "CHECKED" by the Instructor.



(4) Arrange the right-hand page as follows:

Determination of \_\_\_\_\_ in \_\_\_\_\_

Analysis begun: date \_\_\_\_\_

Analysis ended: date \_\_\_\_\_

*Charge 1*

Weight of tube + substance =

Weight of tube - charge = \_\_\_\_\_

Weight of charge =

Weight of crucible + precipitate + ash = \_\_\_\_\_ 1st heating,

" " " " " = \_\_\_\_\_ 2nd heating,

" " " " " = \_\_\_\_\_ 3rd heating,

" " " " " \_\_\_\_\_ etc.

Accepted constant weight of crucible

+ precipitate + ash =

Weight of crucible = \_\_\_\_\_

Weight of precipitate + ash =

Weight of ash = \_\_\_\_\_

Weight of precipitate = \_\_\_\_\_

**CALCULATION**

(See sample calculations)

\_\_\_\_\_ % of \_\_\_\_\_

(5) Make *all* the calculations *in* the book and, as before recommended, use logarithms for calculations.

THE FACTS CONTAINED UNDER "APPARATUS" AND "PROCESSES EMPLOYED IN GRAVIMETRIC ANALYSIS" MUST HAVE BEEN LEARNED BEFORE WORK IN THE LABORATORY IS BEGUN.

---

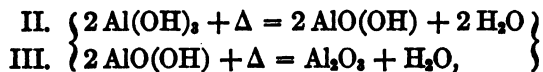
BEFORE BEGINNING EACH NEW DETERMINATION, IT IS ESSENTIAL FOR THE STUDENT BEFORE COMING INTO THE LABORATORY TO HAVE STUDIED AND MASTERED THE PROCESS AND ITS ACCOMPANYING NOTES.

**DETERMINATION OF ALUMINIUM  
IN  
POTASSIUM ALUM,  $KAl(SO_4)_2 \cdot 12H_2O$**

ALUMINIUM is:

- (a) precipitated by ammonium hydroxid,  $NH_4OH$ , as aluminium hydroxid,  $Al(OH)_3$ , in the presence of an ammonium salt,  $NH_4Cl$ ;
- (b) converted by ignition to and weighed as aluminium oxid,  $Al_2O_3$ ;
- (c) calculated as per cent. of aluminium.

**REACTIONS**



or



## DETERMINATION OF ALUMINIUM

A rigid adherence to the minute directions given under "Aluminium" will save time and will give skill in manipulation, an essential to accurate results.

PROCEDURE<sup>1</sup>

On a 350 c.c. beaker (No. 3), which should be covered with a watch glass, place a label marked "Al."

Wipe off the cork and weighing tube containing the salt and replace the cork.

Weigh the tube containing the salt and record the weight on the right-hand page of the notebook.

Hold the weighing tube inclined slightly upwards over the mouth of the beaker and carefully remove the stopper, which, to prevent loss, is held over the dish. Tip the mouth of the tube downwards into the beaker and with slight taps, or rotary motion, remove from the tube an amount sufficient to make a charge of about 1 gram<sup>2</sup> of the salt. Tap down into the tube what-

---

EXPLANATORY FACTS

1. As this is a salt of known composition, each student should check his work by calculating the per cent. of aluminium in  $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ . This calculation must be put *in full* on the left-hand page of the notes.

This determination is not done in duplicate.

2.  $\text{Al}_2\text{O}_3$ , the final substance weighed, is about only one-ninth of the original charge. It is therefore desirable to start with a somewhat large quantity.

ever remains. Replace the cork and weigh again. At all times, in order to avoid moisture from the hands, hold the tube and cork as lightly as possible.

Record the weight under the first entry and subtract to get the weight of the salt to be used for analysis.

Dissolve by pouring on the salt 100 c.c. of hot, distilled water. Dissolving the substance

### PROCEDURE

Add 25 c.c. of a solution of *ammonium\* chlorid*.<sup>3a4</sup>

---

### EXPLANATORY FACTS

3. Metallic hydroxids are not completely precipitated in the presence of tartaric and citric acids, sugar, etc. In such cases, nonvolatile organic matter must be decomposed by adding  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  to the solution, evaporating to dryness, fusing the residue and extracting it with dilute hydrochloric acid.

4. (a) The presence of the ammonium salts (1) insures the complete precipitation of the aluminium hydroxid,  $\text{Al}(\text{OH})_3$ , since such salts cause the reprecipitation of the  $\text{Al}(\text{OH})_3$  which might be dissolved in the excess of the reagent and (2) affects the physical state of the aluminium hydroxid by preventing the formation of a colloidal or semisoluble condition (hydrosol). Boiling alone does not completely change hydrosol into insoluble hydrogel.

(b) It is usually observed that precipitates made from solutions containing large quantities of ammonia salts will, when washed with hot water, become sticky and wash so slowly that it is impossible to free them from the last traces of the salts and also that very perceptible quantities of alumina settle out from such washings and filtrates. It is essential for successful precipitations to avoid such excesses.

\* "Chemistry of the Metals," Experiments Nos. 217 and 218.

Add perfectly clear *ammonium hydroxid* in slight excess,<sup>5</sup> that is, until the odor persists after the solution is stirred. Precipitation of the hydroxid

Cover the beaker with a watch glass and boil gently until the odor of ammonia has nearly disappeared and until red litmus paper held over the solution is only slowly turned blue.<sup>6</sup>

Rinse off the inside of the watch glass into the beaker by means of a jet of hot water from the wash bottle.

While the precipitate is subsiding —

Fold the filter paper exactly into quarters.

Open the paper into a cone and force it into the apex of the funnel.

To complete the fitting process so that there shall be no air spaces<sup>7</sup> between the glass and the paper, fill the funnel with distilled water, let some of it run through the stem, pour out the rest and, where it is necessary, press the paper against the glass.

Place a larger beaker, one of 500 c.c. capacity (No. 4), on a clean piece of filter paper on the base of the filter stand.

Arrange the funnel so that its tip will come just below the curve of the lip of the beaker and touch its side. Filtration of the hydroxid

---

#### EXPLANATORY FACTS

5. Aluminium hydroxid is soluble in an excess of ammonium hydroxid.\*

6. Upon long boiling, by decomposition of the salts, ammonia is liberated and the solution becomes acid.

7. If an air space is left, it destroys the accelerating effect of the weight of water in the long-stemmed funnel, — the reason for having a funnel with so long a stem.

\* "Chemistry of the Metals," Experiment No. 217.

Without delay<sup>8</sup> pour off the supernatant liquid into the filter as follows:—

To avoid spattering, pour down a stirring rod held against the lip of the beaker, so that the stream of liquid will strike the doubled side of the filter paper, not upon the surface of the solution in the funnel. *The level of the liquid should be kept an eighth of an inch below the edge of the paper.*

The entire contents of the funnel should be allowed to run out before more is added. In the long run this saves time.

The mistake should not be made of transferring at the start much, if any, of the precipitate. It should be allowed to settle completely in the beaker and the supernatant liquid, only, be decanted off through the filter paper.

Wash the precipitate in the beaker by decanta-  
tion<sup>9</sup> with hot water.<sup>10</sup> This is accom-  
plished as follows:

Washing the hy-  
droxid by decanta-  
tion

Direct carefully down the rod or sides of the beaker a stream of hot, distilled water from the wash bottle into the precipitate. Stir with a rounded glass rod and allow the precipitate to settle. Pour off the water through the filter.

This washing, settling and filtering should be done three times.

During filtration save time by igniting the crucible according to the directions given on pages 39 and 40.

---

#### EXPLANATORY FACTS

8. Ammoniacal liquids exert a solvent action upon glass.

9. By decantation, a precipitate is washed more thoroughly and in less time than if transferred at once to the filter paper and entirely washed in the funnel.

10. It is sometimes advantageous to have added to the hot water two drops of ammonium hydroxid and two grams of ammonium nitrate per liter (see fact 4 (b)).

As quickly as possible,<sup>11</sup> transfer the precipitate quantitatively to the filter paper. Hold the beaker in the left hand using the forefinger to keep in place the stirring rod which should rest across the top of the beaker, one end touching and extending beyond the lip. With the right forefinger on the movable tip of the wash bottle, direct the stream of water in such a manner as to wash the precipitate from the beaker down the stirring rod into the funnel. When the precipitate is apparently removed, rub the stirring rod clean with the "policeman" or with a closely trimmed goose quill and hot water from the wash bottle. Rub the entire surface of the beaker with the "policeman" aided by a fine stream of hot water. Pour this liquid into the filter. Finally, closely scrutinize the beaker held in a strong light to be sure that it is perfectly clean on the inside. Wash off into the filter any precipitate that may remain on the "policeman."

Wash the precipitate in the funnel with hot water as follows:<sup>12</sup>

Direct the stream of water against the double fold of the paper and then, with a rotary motion of the wash-bottle tip, bring the jet of water out into the mass of the precipitate. Let drain and repeat. Washing the hydroxid in the funnel Before the filtrate is tested for complete washing, the upper edges of the paper should be washed with extreme care. Avoid getting any of the precipitate above the paper level.

---

#### EXPLANATORY FACTS

11. If not done at once, the precipitate will adhere to the beaker and be removed with difficulty.

12. Aluminium hydroxid soon hardens and cracks and therefore should at once be washed completely. Filtration once begun must be finished during the laboratory period.



Test a few drops of the filtrate with *silver nitrate*\* solution for chlorids.<sup>13</sup> The precipitate must be washed till a fresh portion of the filtrate gives no evidence of their presence. As stated above, never completely fill the filter and never add more liquid till the filter has entirely drained.

Test the filtrate with a little more *ammonium hydroxid* to insure complete precipitation.

Cover the funnel with an ordinary 11 cm. filter paper wet with distilled water. Stretch it over the top by pressing the projecting rim of the paper firmly around the outside of the funnel. Tear off the extra paper which hangs below the edge. Enough will remain to hold it on.

Place the covered funnel in an air bath to dry the precipitate. It is possible, with great care, to ignite the precipitate without drying, but it introduces a greater chance of error. It is much better to proceed with other work and return to this when it has dried.

Wash either a platinum or a porcelain crucible thoroughly and dry with an "analytical" towel (pure linen). With a pair of nickel tongs, place the crucible upon a clean pipestem triangle.

---

#### EXPLANATORY FACTS.

13. The reaction at the beginning of this analysis shows the formation of  $K_2SO_4$  and  $(NH_4)_2SO_4$ . These and also the added  $NH_4Cl$  should be completely removed to avoid increasing the weight of aluminium hydroxid. When the absence of chlorids is assured, it may be assumed that the two sulfates are also removed.

\* "Chemistry of the Metals," Experiment No. 49.

For a few minutes, heat the partially covered crucible to redness with a properly adjusted Bunsen flame. Remove the Bunsen. After the redness has died down, with the tongs put the crucible and cover in to the desiccator to cool. On the porcelain plate, next to the hole holding the crucible, there should be pasted a label marked "Al."

After twenty minutes, weigh the crucible and <sup>Weighing the</sup> cover, replace them in the desiccator and <sup>crucible</sup> record the weight.

When the precipitate is dry, leave the cover in the desiccator and put the crucible on a piece of glazed paper. Neither crucible nor cover after having been weighed should be put anywhere but on the desiccator plate, the triangle, glazed paper or on a clean watch glass.

Remove the filter paper from the funnel, fold it carefully and place it with its contents in the base of the crucible. This is not the type of precipitate which is reduced by the carbon of the filter paper; they may, therefore, be ignited together.

If any of the precipitate adheres to the funnel, wipe it off on a small bit torn from the clean, folded portion of the filter paper and put it into the crucible with the main precipitate.

Place the crucible at an angle on the triangle on the lamp stand.

If the dried filter paper is charred with great care, there is no danger of mechanical loss. If, however, for any reason, the precipitate is wet or moist, the crucible should be placed upright and the utmost pains taken not to heat it sufficiently to cause a violent escape of steam, which might drive out some of the precipitate. The ring of the stand should be so adjusted as to bring the crucible above but not touching the flame. When the paper has dried, the crucible may be turned on its side.

Too much care cannot be exercised at this point. The object is to destroy the filter paper by dry distillation and *not to burn it*. Avoid future difficulty by implicitly following these directions. It is possible to place the crucible at such a distance above the flame as to accomplish this end. It is, however, advisable to stand at the work, lamp in hand, with a low flame, ready to withdraw it if the escape

of volatile matter becomes too violent. If, through the inexperience of the student, the paper takes fire, the tongs should be at hand that the lid may be taken from the desiccator and the crucible covered to extinguish the flame. After the escape of vapors has ceased and the filter paper has completely charred, the heat may be increased and the charred paper ignited till the carbon is oxidized.

Heat ten minutes over the blast lamp.<sup>14</sup>

Remove the crucible to the desiccator, the cover of which should be put on with a slight twist, and cool until the crucible has acquired the temperature of the room. A red-hot crucible should not be placed in the desiccator. No great time, however, must elapse between the removal of the lamp and the insertion of the crucible. If the crucible is put in hot enough to expand the air and to lift the cover of the desiccator, the cover should be carefully readjusted.<sup>15</sup> Three facts should be borne in mind: (1) The desiccator always should be kept covered, except at the moment of putting in or taking out the crucible, which, after ignition, should never be handled except with the tongs. (2) The cover of the desiccator unless inverted should never be put down on anything but the desiccator itself. (3) Before weighing, the desiccator and its contents should be put either in the balance room or in a place in which it will acquire the approximate temperature of the balance.

---

#### EXPLANATORY FACTS

14. The final ignition in the blast lamp is to expel the last traces of water and insure complete change to oxid (see reactions II and III).

15. Carefully, because this expansion of the air may have produced a reduced pressure, and the inrush of air may cause some of the precipitate to fly out of the crucible.

Weigh<sup>16</sup> and record weights. Weighing the ignited precipitate  
Repeat heating over blast lamp, cooling and weighing till the weights agree within three-tenths of a milligram. This will bring the substance to a "constant weight."

---

#### EXPLANATORY FACTS

16. Aluminium oxid is hygroscopic and should, therefore, be weighed quickly.

## SAMPLE CALCULATION

Weighing tube and salt = 6.0227 grams  
 Weighing tube — charge = 4.9666 grams  
 Weight of charge = 1.0561 grams

Weight of crucible + ash +  $\text{Al}_2\text{O}_3$  = 11.9108 grams  
 Weight of crucible = 11.7973 grams  
 Weight of ash and  $\text{Al}_2\text{O}_3$  = 0.1135 gram  
 Weight of ash = 0.0001 gram  
 Weight of  $\text{Al}_2\text{O}_3$  = 0.1134 gram

Atomic weight of Al = 27.10  
 “ “ “ O = 16

Molecular weight of  $\text{Al}_2$  = 54.20  
 “ “ “  $\text{Al}_2\text{O}_3$  = 102.20

The ratio of  $\text{Al}_2$  to  $\text{Al}_2\text{O}_3$  =  $\frac{54.20}{102.20} = 0.53033$ .

0.53033 is the constant factor that represents the amount of Al in  $\text{Al}_2\text{O}_3$ .

(Weight of  $\text{Al}_2\text{O}_3$ ) 0.1134 gram multiplied by 0.53033 (the constant factor) = 0.06013 gram of Al in 0.1134 gram of  $\text{Al}_2\text{O}_3$ .

Since there is 0.06013 gram of Al in the original charge of 1.0561 of the salt, then:

$$\frac{0.06013 \times 100}{1.0561} = \underline{\underline{5.69\% \text{ Al}}}$$

## CALCULATION BY LOGARITHMS

The logarithm of the weight of  $\text{Al}_2\text{O}_3$  minus the logarithm of the weight of the original charge plus the logarithm of the constant factor of the amount of Al in  $\text{Al}_2\text{O}_3$  equals the logarithm of the per cent. of Al.

---

Log. of (weight of $\text{Al}_2\text{O}_3$ ) 0.1134	= 9.05461-10
Log. of (original charge) 1.0561	= 0.02366
	<u>9.03095-10</u>
Log. of (constant factor) 0.53033	= 9.72454-10
	<u>18.75549-20 or</u>
	<u>2.75549</u>

Anti-log. of 2.75549 = 0.0569 or 5.69 % Al.

**THE DETERMINATION OF COPPER  
IN  
PURIFIED COPPER SULFATE,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  \***

Copper is:

- (a) precipitated by sodium hydroxid,  $\text{NaOH}$ , as cupric hydroxid  $\text{Cu}(\text{OH})_2$ ;
- (b) converted by boiling and ignition to cupric oxid,  $\text{CuO}$ , a type of precipitate that must be largely removed from the filter paper before ignition;
- (c) weighed as cupric oxid;
- (d) calculated as per cent. of copper.

**REACTIONS**

- I.  $\text{CuSO}_4 + 2 \text{NaOH} = \text{Cu}(\text{OH})_2 + \text{Na}_2\text{SO}_4$ .
- II.  $\text{Cu}(\text{OH})_2 + \Delta = \text{CuO} + \text{H}_2\text{O}$ .
- III.  $\text{CuO} + \text{C} = \text{Cu} + \text{CO}$ .
- IV.  $3 \text{Cu} + 8 \text{HNO}_3 = 3 \text{Cu}(\text{NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO}$ .
- V.  $2 \text{Cu}(\text{NO}_3)_2 + \Delta = 2 \text{CuO} + 4 \text{NO}_2 + \text{O}_2$ .

\* If this course is to be limited to ninety hours, the determination of copper may be omitted. Otherwise, the value of the preparation of a pure from a commercial salt and the practice of the separation of a precipitate from the filter paper before ignition justify the time expended.

**PREPARATION OF THE PURE  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  FROM  
"BLUE VITRIOL" (COMMERCIAL)**

Weigh 50 grams of *commercial copper sulfate* on a rough balance. Dissolve by heating in 150 c.c. of distilled water.

Add 1 c.c. of *dilute nitric acid*<sup>17</sup> and keep the solution boiling gently for fifteen minutes.

Filter and put the beaker containing the filtrate in cold water. Stir vigorously to get finely divided crystals.

Filter, wash the crystals with a small amount of cold water, let drain and dry by pressing gently<sup>18</sup> between a folded sheet of filter paper.

Put the crystals on a clean five-inch watch glass and let dry in the open air. Turn the crystals over frequently with a clean stirring rod until they no longer adhere to the glass.

Transfer the crystals at once to a piece of glazed paper creased through the middle and empty into a test tube that has been fitted with a cork.

---

**EXPLANATORY FACTS**

17. Commercial "blue vitriol" usually contains ferrous sulfate. Ferrous sulfate and copper sulfate tend to crystallize together and cannot, therefore, be separated by "fractional crystallization." The ferrous sulfate is consequently oxidized to ferric sulfate by the nitric acid. The ferric sulfate does not tend to separate with the copper sulfate which is easily obtained in crystals after concentrating the liquid.

18. If pressed roughly, fragments of the paper may mix with the crystals.



## PROCEDURE \*

Fill a weighing tube two-thirds full of the *purified copper sulfate*<sup>19</sup> and fit in a cork.

Weigh into a 250 c.c. casserole, labeled "Cu," one gram of the salt and record the weight. Weighing the charge

Dissolve in 100 c.c. of hot, distilled water. Dissolving the substance  
The solution should be perfectly clear.

Cover the beaker and heat the solution to boiling † (see reaction II).

While stirring with a glass rod having rounded ends, add, drop by drop, a dilute solution of *sodium hydroxid*<sup>20</sup> (see reaction I) in slight excess.<sup>21</sup> Precipitation of the hydroxid

Stir constantly and continue to heat for ten minutes. Keep the beaker covered when possible.

Test for excess of sodium hydroxid by putting a drop of the solution on a strip of red litmus paper with the stirring rod. Wash off the litmus paper into the beaker with a little distilled water from the wash bottle.

## EXPLANATORY FACTS

19. As this is a salt of known composition, each student must check his work by calculating the per cent. of copper in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . This calculation should be put on the left-hand page of the note-book.

20. When cupric hydroxid is first formed it is a greenish blue; it turns brown at once at a boiling temperature and then nearly black. This indicates the change to cupric oxid.

21. Cupric hydroxid is insoluble in excess of fixed alkalies in dilute solution.

\* This determination is not done in duplicate.

† See "Chemistry of the Metals," Experiment No. 102.

Rinse off the underside of the watch glass into the beaker by means of a jet of hot water from the wash bottle.

While the precipitate is settling, fit a filter paper (S. & S. "Ashless," 11 cm.) into a funnel as described on page 36. To collect the filtrate, use a 500 c.c. beaker (No. 4).

After the precipitate has settled, pour off the liquid through the filter. Filtration of the oxid

Carefully direct a stream of hot water from the wash bottle into the precipitate and stir. Washing the oxid

Boil again.<sup>22</sup>

Wash by decantation several times, page 37.

During filtration, start the heating, cooling and weighing of the porcelain crucible, page 39. Preparation of the crucible

Transfer the precipitate quantitatively to the filter paper as described in detail under "The Determination of Aluminium," page 38.

Wash the precipitate in the funnel with hot water until a few drops of the filtrate acidified with *hydrochloric acid* give with *barium chlorid* solution no test for sulfate.\* Direct the stream downwards onto the upper part of the filter. As previously stated, never completely fill the filter paper and wait till it has entirely drained before adding more liquid. Testing the filtrate for complete washing

Cover the funnel with an ordinary 11 cm. filter paper wet with distilled water.

Place the funnel in an oven to dry the precipitate. Drying of the precipitate

This precipitate cannot be ignited *with* the paper as the carbon from the filter paper will reduce copper oxid to metallic copper (see reaction III).

---

#### EXPLANATORY FACT

22. Cupric hydroxid must be completely changed by boiling to cupric oxid.

\* See "Chemistry of the Metals," Experiment No. 232.

Place a perfectly clean three-inch watch glass upon a circular piece of glazed paper about six inches in diameter.

Separate the copper oxid from the filter paper in the following manner: Remove the filter paper from the funnel. Gently loosen the precipitate adhering to the sides of the paper by pressing the funnel-shaped paper with thumb and fingers. With great care empty the bulk of the contents of the filter paper upon the watch glass. Invert the filter paper over the watch glass and gently rub the sides together. Avoid rubbing hard enough to detach threads of the paper. Cover the precipitate with an inverted six-inch watch glass.

Separation of the copper oxid from the filter paper

Wipe off any of the precipitate that has adhered to the glass funnel and drop the bit of paper into the filter-paper cone.

Fold the filter paper, which should be flattened into the shape of a quarter circle, in halves lengthwise, fold once more in the same way. Roll the *top* edge and secure it by fastening around it loosely a platinum wire which will then come into contact with clean paper only.

Preparing and burning the filter paper after the bulk of the precipitate has been removed

Hold the folded filter paper by the wire over the weighed crucible, which should stand on a piece of glazed paper. Burn and let the ash fall into the crucible (see reaction III).

Moisten the residue with one or two drops of *nitric acid* to dissolve it and form cupric nitrate\* (see reaction IV).

Treatment of any reduced oxid

To avoid loss by spattering, heat with great care on a *hot plate* to drive off the excess of nitric acid till the mass is dry (see under "Evaporation of Liquids," page 24).

Place the crucible on its side on a clean, clay triangle on a ring stand and heat first gently and then to redness till the cupric nitrate has changed into black cupric oxid† (see reaction V).

\* See "Chemistry of the Metals," Experiment No. 91.

† See "Chemistry of the Metals," Experiment No. 96.

Remove the lamp and when the crucible is nearly cool, place it on a piece of glazed paper and transfer the main part of the precipitate which is on the watch glass into the crucible.

Brush off the particles remaining on the glass with a small brush or trimmed feather. Finally brush into the crucible any particles that may be on the glazed paper.

Treatment of the  
entire combined  
precipitate

Heat strongly for a few more minutes.

Cool in the desiccator.

Ignition  
cooling, and  
weighing

Weigh and record the weight.

Repeat the heating, cooling and weighing till the weights agree within three-tenths of a milligram, thus bringing the substance to a "constant weight."

## SAMPLE CALCULATION

The per cent. of Cu in  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ .

Weighing tube + copper sulfate = 14.8345 grams

Weighing tube — charge = 13.6405 grams

Weight of charge = 1.1940 grams

Weight of crucible with cover + ash + CuO = 25.4987 grams

Weight of crucible with cover = 25.1190 grams

Weight of ash and CuO = 0.3797 grams

Weight of ash = 0.0002 grams

Weight of CuO = 0.3795 grams

Atomic weight of Cu = 63.60

“ “ “ O = 16.00

Molecular “ “ CuO = 79.60

The ratio of Cu to CuO =  $\frac{63.60}{79.60} = 0.79897 +$  or 0.7990.

0.7990 is the “constant factor” that represents the amount of Cu in CuO.

(Weight of CuO), 0.3795 grams, multiplied by 0.7990 (the constant factor) = 0.30322 gram of Cu in 1.1940 grams of the salt.

$$\frac{0.30322 \times 100}{1.1940} = \underline{\underline{25.39\% \text{ Cu.}}}$$

## CALCULATION BY LOGARITHMS

The logarithm of the weight of CuO minus the logarithm of the weight of the original charge plus the logarithm of the constant factor of the amount of Cu in CuO equals the logarithm of the per cent. of Cu.

$$\begin{array}{rcl}
 \text{Log. of (weight of CuO) } 0.3795 & = & 9.57921-10 \\
 \text{Log. of (original charge) } 1.1940 & = & 0.07700 \\
 & & \hline
 & & 9.50221-10 \\
 \text{Log. of (constant factor) } 0.79900 & = & 9.90255-10 \\
 & & \hline
 & & 19.40476-20 \text{ or} \\
 & & \bar{1}.40476
 \end{array}$$

$$\text{Anti-log of } \bar{1}.40476 = 0.2539 \text{ or } \underline{\underline{25.39\%}}.$$

**DETERMINATION OF IRON  
IN AN  
UNKNOWN, SOLUBLE, FERROUS SALT SIMILAR TO  
FERROUS SULFATE**

Iron is:

- (a) oxidized in the presence of hydrochloric acid to the ferric state by nitric acid,  $\text{HNO}_3$ ;
- (b) precipitated by ammonium hydroxid,  $\text{NH}_4\text{OH}$ , as ferric hydroxid,  $\text{Fe}(\text{OH})_3$ ;
- (c) converted by ignition to, and weighed as, ferric oxid,  $\text{Fe}_2\text{O}_3$ .  
(Type of precipitate which by ignition loses component water);
- (d) calculated as per cent. of iron.

**REACTIONS**

- I.  $6 \text{FeSO}_4 + 8 \text{HNO}_3 = 2 \text{Fe}_2(\text{SO}_4)_3 + 2 \text{Fe}(\text{NO}_3)_3 + 2 \text{NO} + 4 \text{H}_2\text{O}$ .
- II.  $2 \text{FeSO}_4 + \text{NO} = (\text{FeSO}_4)_2\text{NO}$ .
- III.  $\text{Fe}_2(\text{SO}_4)_3 + 6 \text{NH}_4\text{OH} = 2 \text{Fe}(\text{OH})_3 + 3 (\text{NH}_4)_2\text{SO}_4$ .
- IV.  $\text{Fe}(\text{NO}_3)_3 + 3 \text{NH}_4\text{OH} = \text{Fe}(\text{OH})_3 + 3 \text{NH}_4\text{NO}_3$ .
- V.  $2 \text{Fe}(\text{OH})_3 + \Delta = \text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{O}$ .

**ADDITIONAL REACTIONS POSSIBLE IN THE PROCESS**

- VI.  $2 \text{FeSO}_4 + \text{O} = \text{Fe}_2\text{O}(\text{SO}_4)_2$ .
- VII.  $3 \text{Fe}_2\text{O}(\text{SO}_4)_2 + 6 \text{HCl} = 2 \text{Fe}_2(\text{SO}_4)_3 + 2 \text{FeCl}_3 + 3 \text{H}_2\text{O}$ .
- VIII.  $3 \text{Fe}_2\text{O}_3 + \text{C} = \text{CO} + 2 \text{Fe}_3\text{O}_4$ .
- IX.  $2 \text{Fe}_3\text{O}_4 + \text{O} = 3 \text{Fe}_2\text{O}_3$ .
- X.  $\text{Fe}(\text{OH})_3 + 3 \text{NH}_4\text{Cl} + \Delta = \text{FeCl}_3 \text{ (partly volatile)} + 3 \text{NH}_3 + 3 \text{H}_2\text{O}$ .

## DETERMINATION OF IRON

## PROCEDURE

- Weigh into two 350 c.c. beakers (No. 3), two portions of the salt of 1.5 grams each. Weighing the charge
- Dissolve in 100 c.c. of distilled water to which 4 c.c. of *concentrated hydrochloric \* acid* <sup>23</sup> have been added. Dissolving the substance
- Cover the beakers with watch glasses, bring the solution to a boil and add to each 2 c.c. of *nitric † acid*.<sup>24&25</sup> Oxidizing the iron to the ferric state
- Again cover the beakers and keep them at the boiling point for about fifteen minutes. The solutions will now show the presence of ferric salts by the clear yellow or red color

## EXPLANATORY FACTS

23. Unless there is free acid present, ferrous iron will not wholly oxidize and basic ferric salts will precipitate (see reactions VI and VII).

24. The iron must be oxidized (see reaction I) before precipitation as the ammonia does not completely precipitate ferrous salts and, even if it did, such a precipitate, ‡ owing to its tendency to oxidize, would be of indefinite composition.

25. The brown coloration that appears when nitric acid is added is due to the combination of NO with the ferrous sulfate in the solution (see reactions I and II). Upon heating, this compound is destroyed and the nitric oxid escapes.

\* "Chemistry of the Metals," Experiment No. 157.

† "Chemistry of the Metals," Experiment No. 155.

‡ "Chemistry of the Metals," Experiments Nos. 158 and 160.



Test for complete oxidation by adding a drop or two more of *nitric acid* which, if no ferrous iron remains, will produce no further brown coloration (see reaction II).

Allow the solution to cool.

While stirring, add a slight excess of *ammonia*<sup>26,27</sup> (test by the odor). Precipitation of  
ferric hydroxid

Heat to incipient boiling with constant stirring.<sup>28</sup>

Allow the precipitate\* to settle.

With hot water, wash several times by decantation through the filter into a 500 c.c. beaker.

Transfer all of the precipitate to the filter paper and wash with hot water<sup>29,30</sup> until a few drops of the filtrate no longer give a test for HCl with  $\text{AgNO}_3$  solution.† Filtration of the  
hydroxid  
  
Washing the  
hydroxid

---

#### EXPLANATORY FACTS

26. Unless all the iron is precipitated as quickly as possible throughout the solution,  $\text{SO}_4$  is lost, as basic ferrous sulfate, by being "dragged down" in neutral zones.

27. The first action upon the addition of ammonia is the neutralization of the free acid in the solution, which results in the formation of ammonium nitrate and ammonium chlorid.

28. In distinction from chromium and aluminium hydroxid, ferric hydroxid is practically insoluble in an excess of ammonia.

29. Ferric hydroxid may be changed to ferric chlorid if heated with any ammonium chlorid that has been left by insufficient washing. As ferric chlorid is somewhat volatile this would result in a loss of iron (see reaction X).

30. In order to avoid the solvent action of ammonia upon the glass, filtration must be begun at once after the precipitate has settled. Once begun, the filtration and washing must be completed without delay.

\* "Chemistry of the Metals," Experiment No. 167.

† "Chemistry of the Metals," Experiment No. 49.

Dry the precipitate in the oven and ignite to a constant weight.<sup>31 & 32</sup> There should not be a greater variation than three-tenths of a milligram. Drying, igniting and weighing the precipitate  
Make the final ignition in a covered crucible over a blast lamp.  
Report the per cent. of iron.

---

#### EXPLANATORY FACTS

31. Proper ignition of the precipitate (see reaction V) changes it to  $\text{Fe}_2\text{O}_3$ . Under reducing conditions, however, reaction VIII may take place and form  $\text{Fe}_3\text{O}_4$  or even metallic iron. If sufficient air is admitted to the crucible during ignition, both of these products will change to  $\text{Fe}_2\text{O}_3$  (see reaction IX).

Reaction V is not completed without the use of the blast lamp.

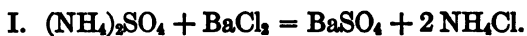
32.  $\text{Fe}_2\text{O}_3$  is hygroscopic: to avoid the absorption of water, it should be weighed as quickly as possible.

**DETERMINATION OF THE ACID RADICAL  $\text{SO}_4$   
IN AN  
UNKNOWN, SOLUBLE, FERROUS SALT SIMILAR TO  
FERROUS SULFATE**

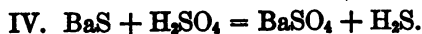
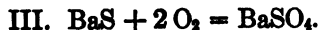
$\text{SO}_4$  is:

- (a) precipitated in the presence of hydrochloric acid by barium chlorid,  $\text{BaCl}_2$ , as barium sulfate,  $\text{BaSO}_4$ ;
- (b) weighed as barium sulfate,  $\text{BaSO}_4$ ;
- (c) calculated as per cent. of  $\text{SO}_4$ .

**REACTION**



**ADDITIONAL REACTIONS POSSIBLE IN THE PROCESS**



DETERMINATION OF THE ACID RADICAL  $\text{SO}_4$ 

## PROCEDURE

Add *hydrochloric acid* in slight excess to the filtrate from ferric hydroxid.<sup>33</sup>

On a water bath, evaporate<sup>34</sup> this solution to dryness in a six-inch evaporating<sup>35</sup> dish (see "Evaporation of Liquids," page 24). Cover with a watch glass which should rest, not upon the rim of the dish, but upon a glass triangle made of bent stirring rod. This allows steam to escape, *Evaporation of* catches the spatters and prevents dust from *the filtrate* falling in.

## EXPLANATORY FACTS

33. It was necessary to precipitate the iron before the determination of sulfur, as (1) the iron tends to contaminate the sulfate and (2) barium sulfate is slightly soluble in ferric chlorid.

34. During evaporation, both the nitric and the hydrochloric acids are decomposed and volatilized. Should any nitric acid remain the barium salt of this acid would form and contaminate the precipitate and the final per cent. would be too high. Nitrates of the alkalies and iron are also particularly liable to be dragged down with barium sulfate.

35. Evaporation is hastened by increasing the top surface of the heated liquid. Broad, shallow dishes, then, are more suited to evaporations than those that are high and narrow.

Rapid evaporation may be obtained by blowing a gentle current of warm, dry air onto the surface of the liquid.

Dissolve the residue in 100 c.c. of water and, if necessary, filter the solution. This evaporation is to remove the nitric acid which is here in the form of ammonium nitrate<sup>36</sup> and which, in the previous process, was used to oxidize the iron (see reaction I under "The Determination of Iron").

Transfer quantitatively to a beaker and add 5 c.c. of dilute hydrochloric<sup>37</sup> acid.

Heat the covered solution to boiling<sup>38</sup> and, while stirring, add slowly,<sup>39</sup> drop by drop, Precipitation of the barium sulfate

---

#### EXPLANATORY FACTS

36. Barium sulfate possesses the quality of dragging down with it compounds, even those that are ordinarily soluble. These are not easily removed by washing and, therefore, lead to inaccurate results.

37. (a) As hydrochloric acid, even when it is dilute, dissolves some barium sulfate, only the smallest excess is added. The presence of an excess of  $\text{BaCl}_2$  lessens this solubility; a *large* excess, however, should be avoided as there is danger, especially if the reagent is added quickly, of some of it being precipitated with the barium sulfate.

(b) When sulfuric acid is precipitated by barium chlorid, some of the chlorid is often "dragged down" by the barium sulfate. As barium sulfate is *somewhat* soluble, these two sources of error under favorable conditions almost counteract each other.

38. Barium sulfate formed in hot acid solution is in the best condition to be retained by the filter paper. If the solution and the barium chlorid were cold, there would be formed a finely divided precipitate which would have to stand hours before it could be filtered.

39. If the reagent is added quickly, barium chlorid as well as barium sulfate will be precipitated.

not exceeding 5 c.c. per minute, a moderate excess of boiling *barium chlorid* \* *solution*.<sup>40</sup>

After the precipitate has settled, add a few more drops of *barium chlorid*. Keep the liquid nearly at the boiling point and stir occasionally during one-half hour or more.

Test for complete precipitation by again adding a few drops of the *barium chlorid*.

Pour the supernatant liquid through a special filter,<sup>41</sup> disturbing the precipitate as little as possible. Filtration of the sulfate

Wash the precipitate twice by decantation with hot water acidified with hydrochloric acid. Then wash with hot water alone and transfer the precipitate to the filter. Washing the sulfate

Wash till the filtrate gives with *silver nitrate* no reaction for chlorids.<sup>42</sup> The filtrate must be clear. Testing the filtrate for complete washing

---

### EXPLANATORY FACTS

40. A soluble barium salt, like barium chlorid, or a soluble sulfate, makes the barium sulfate less soluble. For this reason, it is desirable to have an excess of barium chlorid, but as barium chlorid is carried down with barium sulfate, a large excess should be avoided.

41. Some of the barium sulfate may run through an ordinary filter.

42. The absence of chlorids proves that the washing is complete.

\* "Chemistry of the Metals," Experiment No. 232.

Dry in the oven,<sup>43</sup> ignite<sup>44</sup> and weigh. Before the second ignition add one drop of *concentrated sulfuric acid*. Be sure that a constant weight is reached. Drying, ignition  
and weighing

Make the final ignition, with the cover on, over the blast lamp.

---

#### EXPLANATORY FACTS

43. With proper precautions this precipitate can be ignited without putting it into the drying oven (see under "Ignition to a Stable Compound," page 25, also pages 39 and 40).

44. Ignite slowly to properly burn the filter paper. Barium sulfate at a high temperature may be reduced by the carbon of the filter paper to barium sulfid. Although sufficient air will usually change the sulfid back to sulfate, the change is sure to take place if sulfuric acid is added.

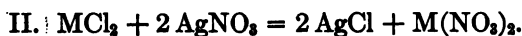
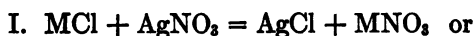
**DETERMINATION OF CHLORIN \*  
IN  
AN UNKNOWN, SOLUBLE CHLORID**

*(Corresponding to the general formula  $MCl$  or  $MCl_2$ )*

Chlorin is:

- (a) precipitated by silver nitrate,  $AgNO_3$ , as silver chlorid,  $AgCl$ ,† a type of precipitate which must be removed from the filter paper before ignition;
- (b) weighed as silver chlorid;
- (c) calculated as per cent. chlorin.

**REACTIONS**



\* Reversed, except in certain special cases, this process may be used for the determination of silver in alloys, etc.

† Unless it fuses,  $AgCl$  is unchanged by ignition, but if it is in contact with the filter-paper when it is ignited, it is reduced by the carbon of the filter paper to metallic silver. Therefore the bulk of the  $AgCl$  is removed from the paper, which is burned separately.



## DETERMINATION OF CHLORIN

All silver precipitates and filtrates containing silver salts are to be put into a side-shelf bottle marked "Silver Residues."

PROCEDURE <sup>45</sup>

Weigh into two 350 c.c. beakers two portions of the chlorid, 0.3 of a gram each.	Weighing the charge
Dissolve in 100 c.c. of cold distilled water. <sup>46</sup>	Dissolving the substance
Add 3 c.c. of <i>dilute nitric</i> <sup>a</sup> <i>acid</i> (sp. gr. 1.2).	

## EXPLANATORY FACTS

45. In this determination avoid exposure to bright light. It changes the silver chlorid from white to violet, which shows a decomposition to a lower chlorid with a loss of chlorin.

Although later, when the hydrochloric and nitric acids are added, any chlorin that has been lost is replaced (see explanatory fact 52), it is as well to avoid the necessity of correcting previous error.

46. Silver chlorid is almost insoluble in cold water, but more soluble in hot water.

47. Nitric acid (1) decreases the solubility of silver chlorid, (2) keeps in solution any other compounds that might be carried down with the silver chlorid and (3) overcomes the tendency which silver chlorid has in cold water of changing to a colloidal state, a condition in which the precipitate will pass through the filter.

The amount of nitric acid is limited to this amount as silver chlorid is somewhat soluble in concentrated nitric acid.

Add *silver nitrate solution*, drop by drop, with constant stirring, until there is no further precipitation.\*

There should be a slight excess of the silver nitrate.<sup>48</sup>

Precipitation of the chlorid

Heat nearly to the boiling point<sup>49</sup> and stir constantly until the precipitate has coagulated and the liquid is clear.

Place the solution in a dark place to settle.

Use filter papers 9 cm. in diameter.

Pour the liquid through the filter without greatly disturbing the precipitate.

Filtration of the silver chlorid

Catch the filtrate in a 500 c.c. beaker.

Wash the precipitate in the beaker three times with cold water slightly acidified with *nitric acid*<sup>50</sup>, decanting the liquid through the filter.

Washing the chlorid

---

### EXPLANATORY FACTS

48. An excess of silver nitrate, as in the case of nitric acid, decreases the solubility of silver chlorid and aids in the coagulation of the precipitate.

If the precipitate is not flocculent there is probably not a sufficient excess of silver nitrate.

49. Do not heat to boiling before the silver nitrate is added in excess, as some of the unprecipitated chlorin might be liberated from the original salt (KCl, NaCl, etc.) by the action of the hot nitric acid.

The heat is necessary to make all the precipitate flocculent.

50. Nitric acid prevents the coagulated precipitate from returning to a colloidal state.

\* "Chemistry of the Metals," Experiment No. 49.

Transfer the precipitate to the filter and continue the washing with cold water acidified with nitric acid until a drop of hydrochloric acid in 3 c.c. of the wash water shows no turbidity.<sup>51</sup> Be sure to wash the filter paper clean above the precipitate.

Testing the filtrate for complete washing

Wash twice with cold water or a mixture of alcohol and water, half and half, to remove the nitric acid. Test for the absence of nitric acid with litmus paper. Save the filtrate for silver recovery.

Dry the precipitate in the oven at 100° C. This precipitate cannot be ignited with the filter paper, as the carbon from the paper will reduce silver chlorid to metallic silver.

Drying the precipitate

Place a perfectly clean three-inch watch glass upon a circular piece of glazed paper about six inches in diameter.

Separate the silver chlorid from the filter paper in the following manner: Remove the filter from the funnel. Gently loosen the precipitate adhering to the sides of the paper by pressing the funnel-shaped paper with the thumb and fingers. With great care, empty the contents of the filter paper upon the watch glass. Invert the filter paper over the watch glass and carefully rub the sides together. Avoid rubbing hard enough to detach threads of the paper. Cover the precipitate with an inverted six-inch watch glass.

Special precautions in regard to ignition of the silver chlorid

---

### EXPLANATORY FACT

51. Mixed with the AgCl are nitrates of the alkali metals that were in combination in the original salt and nitrate of silver. The absence of the latter in the HCl test indicates that the other soluble nitrates are also washed away.

After removing the precipitate, press the filter paper into the shape of a quarter circle, fold in halves lengthwise, fold once again in the same way. Roll the top edge and secure it by fastening around it loosely a platinum wire. If there is any silver chlorid on the edge of the paper the heat will reduce it to metallic silver, which will alloy with the platinum. This will break the wire and spoil the determination as well.

Hold the folded filter paper by the wire over a weighed porcelain crucible, which should be on a piece of glazed paper. Burn and let the ash fall into the crucible.

Place the crucible on its side on a clay triangle. As silver chlorid volatilizes at rather a low temperature, apply the Bunsen flame only on that part of the crucible upon which there rest particles of Ignition of the chlorid carbonaceous matter. When these have whitened, remove the lamp and cool the crucible.

Add to the ash two drops of *concentrated nitric acid* to dissolve the metallic silver\* and then two drops Treatment of any reduced silver of *concentrated hydrochloric acid* to convert it to the chlorid.

Evaporate to dryness on the water bath.

Transfer the main part of the precipitate which is on the watch glass into the crucible. Hold the watch glass over the glazed paper and brush off into the crucible the remaining particles with a small brush or trimmed feather. Finally brush into the crucible any particles that may be on the glazed paper.

Add to the precipitate two drops of *concentrated nitric acid* and two drops of *concentrated hydrochloric* <sup>52</sup> *acid*.

---

#### EXPLANATORY FACT

52. It is at this point that the silver chlorid which has been reduced to metallic silver by sunlight is dissolved and changed back to the chlorid

\* "Chemistry of the Metals," Experiment No. 46.

Evaporate to dryness on the water bath.

Heat with great care until the silver chlorid barely begins to fuse at its edges.<sup>53</sup> If it is heated too strongly the determination will be ruined.

Cool and weigh.

Weighing the  
chlorid

Heat, cool and weigh until a constant weight is obtained.

---

#### EXPLANATORY FACT

53. Silver chlorid slightly decomposes and volatilizes at its temperature of fusion, 460° C.

**DETERMINATION OF CALCIUM AND MAGNESIUM  
IN  
MIXED CARBONATES<sup>54</sup>**

1. The soluble constituents are dissolved from the mineral, the solution is evaporated to dryness and the residue dehydrated. This leaves insoluble siliceous matter.

2. Iron and aluminium are precipitated by ammonium hydroxid,  $\text{NH}_4\text{OH}$ , as ferric hydroxid,  $\text{Fe}(\text{OH})_3$ , and aluminium hydroxid,  $\text{Al}(\text{OH})_3$ .

3. Manganese, if present, is precipitated by ammonium hydroxid, after oxidation with bromin, as an oxid of varying composition.

1, 2 and 3 are not weighed. They are simply to be removed and rejected before the calcium and magnesium are precipitated.

4. Calcium is:

- (a) precipitated by freshly prepared ammonium oxalate solution  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ; as calcium oxalate,  $\text{CaC}_2\text{O}_4$ ;
- (b) changed by ignition to calcium oxid and weighed as such;
- (c) calculated as per cent. calcium oxid.

5. Magnesium is:

- (a) precipitated by microcosmic salt,  $\text{NaNH}_4\text{HPO}_4$ , as crystalline magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4$ ;
- (b) changed by ignition to magnesium pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ , and weighed as such;
- (c) calculated as per cent. of magnesium oxid.

---

**EXPLANATORY FACT**

54. Such a mixture is found in dolomite (magnesium limestone). This is one of the common minerals whose composition is  $\text{CaCO}_3 \cdot \text{MgCO}_3$  in varying proportions. It may also contain manganese, aluminium, iron, silica, etc.

## REACTIONS

*Calcium and Magnesium*

- I.  $\text{CaCO}_3 + 2 \text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2.$
- II.  $\text{MgCO}_3 + 2 \text{HCl} = \text{MgCl}_2 + \text{H}_2\text{O} + \text{CO}_2.$
- III.  $\text{H}_4\text{SiO}_4 + \Delta = 2 \text{H}_2\text{O} + \text{SiO}_2.$
- IV.  $\text{CaCl}_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 = \text{CaC}_2\text{O}_4 + 2 \text{NH}_4\text{Cl}.$
- V.  $\text{CaC}_2\text{O}_4 + 2 \text{HCl} = \text{CaCl}_2 + \text{H}_2\text{C}_2\text{O}_4.$
- VI.  $\text{CaCl}_2 + \text{H}_2\text{C}_2\text{O}_4 + 2 \text{NH}_4\text{OH} = \text{CaC}_2\text{O}_4 + 2 \text{NH}_4\text{Cl} + 2 \text{H}_2\text{O}.$
- VII.  $\text{CaC}_2\text{O}_4 + \Delta = \text{CaO} + \text{CO}_2 + \text{CO}.$
- VIII.  $\text{MgCl}_2 + \text{NaNH}_4\text{HPO}_4 = \text{MgHPO}_4 + \text{NaCl} + \text{NH}_4\text{Cl}.$
- IX.  $\text{MgHPO}_4 + \text{NH}_3 = \text{MgNH}_4\text{PO}_4.$
- X.  $2 \text{MgNH}_4\text{PO}_4 + \Delta = \text{Mg}_2\text{P}_2\text{O}_7 + 2 \text{NH}_3 + \text{H}_2\text{O}.$

## DOLOMITE

## PROCEDURE

Weigh into 350 c.c. beakers two portions of the finely ground mineral of 1.5 grams each. Weighing the charge

REMOVAL OF THE SILICEOUS MATTER<sup>55</sup>

Treat in covered beakers with *hydrochloric acid*\* Dissolving the substance  
(1.12 sp. gr.) until action ceases (see reactions I and II).

Transfer quantitatively into evaporating dishes and evaporate to dryness on a water bath. Dehydration of the silicic acid

Heat for two hours at 130° C. (see reaction III).

Cool and add to the residue a few drops of *concentrated hydrochloric acid*.

---

EXPLANATORY FACT

55. The siliceous residue, composed of quartz, clay, etc., is largely insoluble in the dilute acid. Some soluble silicic acid may, however, pass into solution. It must be heated at 130° C. to change it to insoluble silica, SiO<sub>2</sub>, which can be filtered off.

The mineral could be dissolved directly in an evaporating dish but it is somewhat easier to judge of cessation of solution if the action takes place in glass.

\* "Chemistry of the Metals," Experiment No. 240.



Warm cautiously and then add 20 c.c. of *hydrochloric acid* (1.12 sp. gr.) and 20 c.c. of water.

While warm, filter into a beaker.

Wash the residue on the filter paper with hot water till it is free from hydrochloric acid, when it may be rejected.

Removal of the  
siliceous residue

#### REMOVAL OF ALUMINIUM<sup>56</sup> AND IRON<sup>57</sup> (AND MANGANESE)

If a qualitative test has shown the presence of manganese,<sup>58</sup> it is precipitated at this point by adding *bromin water* to the filtrate from the silica till a permanent yellow color remains. Then proceed with the addition of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  as in the following paragraph.

Removal of iron,  
aluminium and  
manganese

If manganese is absent add a few drops of *nitric acid* to the filtrate from the silica and boil to be sure that the iron is all oxidized. Add the least possible excess of *ammonium hydroxid*. Gently boil the solution till it is but faintly ammoniacal.

Quickly<sup>59</sup> filter the precipitated iron and aluminium hydroxid (and perhaps manganese) and wash three or four times with hot water.

Mark the filtrate and washings "A."

---

#### EXPLANATORY FACTS

56 and 57. See notes under aluminium and iron determinations.

58. It is necessary to add bromin to oxidize the manganese, which, with ammonia, forms a hydrated dioxid. This hydrated dioxid of manganese is thus removed with the iron and alumina.

59. Filter quickly to avoid action of ammonia upon the glass and also to avoid the absorption of carbon dioxid.

Dissolve<sup>60</sup> the precipitate of iron, aluminium (and manganese) on the filter paper with hot, dilute *hydrochloric acid*, receiving this solution in a separate beaker.

Solution of the iron, aluminium and manganese precipitates

Thoroughly wash the acid solution out of the paper.

Test washings with litmus paper.

If manganese is not present, add a slight excess of *ammonia water* to reprecipitate the iron and aluminium from this acid solution.

Reprecipitation of the iron, aluminium and manganese

If manganese *is* present, again add a few drops of bromine water before adding the ammonia.

Boil till only faintly ammoniacal.

Filter and wash free from chlorids. Reject the precipitate.

Mark the filtrate and washings "B."

---

#### EXPLANATORY FACT

60. This re-solution and reprecipitation is necessary to completely separate the small quantity of calcium which may have precipitated as carbonate, due to absorption of atmospheric  $\text{CO}_2$  by the alkaline solution.

## DETERMINATION OF THE CALCIUM

This element is now contained in the filtrate and washings "A" from the original iron and aluminium precipitate and in the filtrate and washings "B" from the second precipitation of iron and aluminium (and possibly of manganese).

Combine the filtrates "A" and "B" and heat to boiling.

Evaporate to 250 c.c. if it exceeds this volume.

Make alkaline with *ammonium hydroxid*.

To the boiling ammoniacal liquid, add slowly, with stirring, a moderate excess of warm, freshly prepared<sup>61</sup> *ammonium oxalate*<sup>62</sup> solution \* (see Precipitation of the calcium oxalate reaction IV).

Heat to boiling for a few minutes and let the precipitate settle for half an hour or more.

Decant the liquid, but do not remove the precipitate to the filter, as it is to be redissolved.

Wash the precipitate by decantation three or four times with hot water till free from ammonium chlorid, Washing by decantation testing the wash water with *silver nitrate* acidified with nitric acid.

## EXPLANATORY FACTS

61. Ammonium oxalate decomposes slowly and ammonium carbonate is one product of this decomposition.

62. Calcium oxalate is somewhat dissolved by magnesium chlorid solution; therefore, enough ammonium oxalate should be added to convert to oxalate the magnesium as well as the calcium.

\* "Chemistry of the Metals," Experiment No. 242.

Test the filtrate for complete precipitation with a few drops of *ammonium oxalate* and let it stand. This filtrate, when combined with the filtrate obtained from the reprecipitated calcium oxalate (see below), if perfectly clear, is ready for the magnesium determination.

Treatment of the filtrate preparatory to the precipitation of the magnesium

Without delay, slightly acidify the filtrate, to prevent the solvent action of the alkali upon the glass.

If the filtrate is more than 150 c.c. in volume, evaporate it on the water bath. The precipitate, if the original sample contained much magnesium, will contain some magnesium oxalate with the calcium oxalate.

Purify<sup>63</sup> the calcium oxalate as follows: redissolve the precipitate on the filter and in the beaker by pouring warm, dilute *hydrochloric acid* (see reaction V) four or five times through the filter into the beaker containing the precipitate. After the calcium oxalate is all dissolved, wash the filter with *ammonium hydroxid*. Dilute the solution to about 250 c.c. Heat and make it slightly alkaline with *ammonium hydroxid* (see reaction VI). Add 5 c.c. of the *ammonium oxalate* solution<sup>64</sup> and let it stand for at least half an hour.

Purification of the first calcium oxalate precipitate

---

#### EXPLANATORY FACTS

63. Although magnesium oxalate is relatively soluble, especially in the presence of ammonia salts, yet as calcium oxalate may drag down some magnesium oxalate, a re-solution and reprecipitation is necessary. On second precipitation, there is relatively so little magnesium present that none of it is contained in the calcium oxalate precipitate.

64. This ammonium oxalate is added to insure the presence of an excess of the reagent, the best condition for the precipitation of the calcium.

Filter through the *same filter paper* as used before.

Filtration and washing of the reprecipitated calcium oxalate

Wash the precipitate with hot water.

Test the filtrate for chlorids and, when the precipitate is free, slightly acidify the filtrate and add it to the first filtrate containing the bulk of the magnesium oxalate. The combined filtrates should not exceed 200 to 300 c.c.

Dry the precipitated calcium oxalate in the oven.

Ignite in a platinum<sup>65</sup> crucible. Heat strongly for about ten minutes.

Drying, ignition and weighing

Finish with a blast lamp for ten minutes<sup>66</sup> (see reaction VII).

Repeat until a constant weight is obtained.

---

#### EXPLANATORY FACTS

65. A higher temperature than that which is needed by many precipitates is required for the complete conversion of the calcium oxalate to calcium oxid. Although a porcelain crucible may be used, in this case one of platinum is better.

66. Weigh quickly, as calcium oxid absorbs moisture from the air.

## DETERMINATION OF MAGNESIUM

## METHOD OF WOLCOTT GIBBS

Concentrate<sup>67</sup> the filtrates containing the magnesium (and ammonium) salts to about 200 c.c. and bring to a boil.

Add to the almost boiling solution several drops of *methyl orange* and, to make neutral, add *ammonia*, drop by drop, till the solution just becomes yellow. Keep hot.

Add a normal solution of *microcosmic salt*,  $\text{NaNH}_4\text{PO}_4$ ,\* till no further precipitation takes place<sup>68</sup> (see reaction VIII). Precipitation of the magnesium ammonium phosphate

While stirring, add a volume of ten per cent. *ammonia* equal to one-third that of the hot solution<sup>69</sup> (see reaction IX).

---

EXPLANATORY FACTS

67. If during concentration any magnesium oxalate settles out, decant the liquid into another beaker, dissolve the salt in dilute hydrochloric acid and combine.

68. Almost ninety per cent. of the magnesium present is *at once* thrown down as amorphous magnesium hydrogen phosphate,  $\text{MgHPO}_4$ .

69. The addition of ammonia and the stirring transform the magnesium hydrogen phosphate into crystalline magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4$ . Simultaneously the remaining magnesium is almost completely thrown down. The complete precipitation is effected upon standing two or three hours.

\* "Chemistry of the Metals," Experiment No. 260.

Let stand two or three hours to insure complete precipitation.

Decant the liquid through the filter.

Wash the precipitate three times by decantation with a wash water made by mixing one part of ammonia (sp. gr. 0.96) and five parts of water. Filtering and washing the magnesium ammonium phosphate

Transfer to the filter and wash till the filtrate gives with *silver nitrate* no reaction for chlorids.

Dry in the hot closet.

Transfer the bulk of the dried precipitate to a weighed porcelain crucible.

Burn the filter paper in a platinum wire spiral and add the ash to the precipitate in the crucible.

Heat the covered crucible very gently until the ammonia is driven off and the precipitate is white.

Then heat <sup>70</sup> more strongly (see reaction X). Ignition, cooling and weighing

Cool in a desiccator.

Ignite to a constant weight. Use the blast lamp if necessary.

---

#### EXPLANATORY FACT

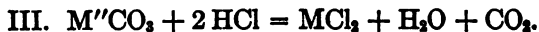
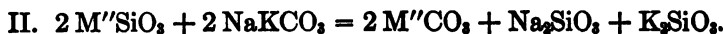
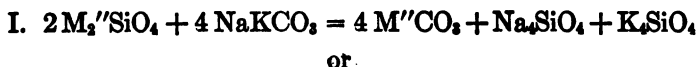
70. During this ignition, great care should be used to avoid the reduction of the pyrophosphate.

**DETERMINATION OF SILICA,  $\text{SiO}_2$ ,  
IN  
GLASS OR OTHER INSOLUBLE SILICATES**

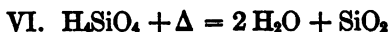
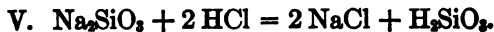
The silicate is:

- (a) converted by fusion with an alkali carbonate into a form decomposable by hydrochloric acid. The metals are converted to carbonates while the silicic acid forms silicates of potassium and sodium.
- (b) dissolved in hydrochloric acid with formation of chlorides and free silicic acid.
- (c) silicic acid is dehydrated to silica,  $\text{SiO}_2$ .
- (d) filtered, ignited, weighed and calculated as silicon dioxide,  $\text{SiO}_2$ .

**REACTIONS**



or



or





## DETERMINATION OF SILICA

## PROCEDURE

Grind the mineral in an agate mortar to an impalpable powder.

The correctness of the determination depends upon this being perfectly done. Grinding and weighing the charge

Weigh into platinum crucibles two portions of the substance, 0.2 of a gram each.

Add 2 grams of *sodium potassium carbonate*,  $\text{NaKCO}_3^{71}$  to each and mix. To avoid loss by frothing,<sup>72</sup> the crucible should never be filled more than one-half full. The carbonate can be added in small portions during the fusion. Fusion with an alkali carbonate

Heat gently until the frothing ceases. When melted, heat for fifteen minutes or longer over a blast lamp until tranquil fusion results.

## EXPLANATORY FACTS

71. By this fusion all the insoluble substances are transformed into such compounds as carbonates, silicates of the alkalies, etc., which are all decomposed by hydrochloric acid. The final solution, then, is composed of chlorids of those metals present and silicic acid. According to the amount present, the silicic acid is wholly or in part in solution.

72. The frothing is caused by the evolution of the carbon dioxide gas.

After the lamp has been removed and when the crucible is just below redness, cool suddenly <sup>73</sup> by placing it on an inverted porcelain mortar, or stone desk-top.

When thoroughly cooled, invert the crucible on a piece of glazed paper and remove the fused cake.

Place the crucible with its adhering pieces of the fused mass and its cover in a beaker.

Add 100 c.c. of water, cover, warm and from time to time add a little *dilute hydrochloric acid* till all of the adhering substance is dissolved. Preparation of the solution

Remove the crucible and its cover with a stirring rod and carefully wash them both off into the beaker.

Put the fused cake from the glazed paper into the beaker and dissolve it with about 50 c.c. of *hydrochloric acid* (sp. gr. 1.12). Keep the beaker closely covered to avoid loss from effervescence.<sup>74</sup>

Transfer the acid solution to an evaporating dish or casserole and evaporate to dryness on a steam bath.

Heat in a hot closet at 130° C. for two hours (see reactions VI & VII). Dehydration of the silicic acid

Cool and add a few drops of *concentrated hydrochloric acid*.

Warm cautiously. To the warm solution add 20 c.c. of *hydrochloric acid* (sp. gr. 1.12) and then 20 c.c. of water. Again warm gently. Filtration and washing of the silica

While warm, filter into a beaker.

#### EXPLANATORY FACTS

73. This loosens the mass from the side of the crucible.

74. Silicic acid, which is slightly soluble in water and in acids, is a white gelatinous mass. It appears yellow as it is suspended in a yellow solution.

Wash the residue on the filter paper till free from hydrochloric acid.

Dry, ignite in a platinum crucible and weigh.<sup>75</sup>

Ignition and weighing

---

#### EXPLANATORY FACT

75. After a constant weight has been obtained, a test of the purity of the silica consists in volatilizing the silica with hydrofluoric acid, HF (see reaction VIII). The silicon tetrafluoride formed volatilizes, while compounds of any admixed metals, if present, remain in the crucible. Deduction of the weight of this nonvolatile residue from the constant weight of silica obtained, gives the weight of the pure silica.



## **SECTION II**

---

### **ELECTROLYTIC ANALYSIS**



## ELECTROLYTIC ANALYSIS.

---

### Ionization

WHEN most compounds are dissolved, their molecules are dissociated, breaking down into *ions*, and the process is called *ionization* or *dissociation*.

*Ions* are electrically charged and in this respect differ from atoms or molecules.

A molecule of common salt, NaCl, is composed of atoms of sodium and chlorine, each of which has its definite characteristics. When these atoms of sodium and chlorine become electrically charged and have become ions, their characteristics have changed. Metallic sodium decomposes water and forms sodium hydroxid, but if this same sodium becomes ionized, it exists in water without chemical change. When this ion loses its electric charge, it immediately decomposes the water, forms sodium hydroxid and liberates hydrogen.

That these ions are electrically charged can be demonstrated. Two conducting plates acting as *electrodes*, the poles of an open electric circuit, one positive and the other negative, are immersed in a dilute solution of common salt. Immediately the sodium is attracted to the negative pole. The negative pole loses some of its negative charge and, it is supposed, neutralizes the positive charge of the sodium ion, which assumes the atomic state and shows the characteristics of metallic sodium by decomposing water to form sodium hydroxid. The chlorine is attracted to the positive

pole which loses some of its charge of positive electricity, presumably neutralizing the negative charge of the chlorin ion. The chlorin escapes at the positive pole and has all the characteristics of chlorin in its ordinary state.

A solution of a dissociated substance is called an *electrolyte*. The greater the dilution the more complete the dissociation.

### Electrolysis

The process of decomposition of a chemical compound in solution by the electric current is called *electrolysis*. The compound is decomposed into two parts, each of which may be simple, like copper, Cu, or complex, like  $\text{SO}_4$ .

Hydrogen or metallic ions formed in solution by dissociation and charged with plus electricity are attracted to the negative pole or *cathode* and are therefore called *cations*.

Nonmetallic ions formed in solution by dissociation and charged with negative electricity are attracted to the positive pole or *anode* and are therefore called *anions*.

The current passes through the liquid between the two metallic surfaces, — electrodes. These may be plates, spirals, cones, etc., according to the method to be employed. They may be fixed or arranged to rotate. The current enters by the positive pole, the anode, and leaves by the negative pole of the circuit, the cathode. The anions separate at the anode and the cations at the cathode.

In the following determination the metals silver and copper are cations and are therefore separated at and deposited on the cathode. The acid radical of the nitrates separates at the anode.

*Current density* is the proportion of the strength of the current to the electrode surface and is usually expressed by amperage per 100 sq. cm. In the potassium cyanid solution used here (see p. 88) the approximate current density used for silver is 2.5 volts and 0.06–0.1 ampere per 100 sq. cm. and that of copper is 5 volts and 1 ampere.

Silver is thus first deposited and then the copper is determined in the remaining solution by using a higher current density. The



metals are deposited on weighed electrodes and the per cent. determined by the observed increase in weight.

Such processes save time, are cleaner and lend themselves to easier manipulation than is the case with ordinary gravimetric methods. The use of electrolysis for analysis is rapidly increasing. The following is but one of the many now established for the separation and determination of metals alone or in the presence of others.

**THE ELECTROLYTIC SEPARATION\***  
**OF**  
**COPPER AND SILVER†**

*A Type of Electro-Analysis*

- (a) The alloy is dissolved in nitric acid, forming nitrates of silver and copper.
- (b) The excess of nitric acid is removed by evaporation.
- (c) An excess of potassium cyanid is added.
- (d) With proper strength of current, the silver is deposited on a weighed platinum electrode.
- (e) With the proper strength of current, the copper is deposited on a similar electrode.

**REACTIONS**

- I.  $\text{Ag} + 2 \text{HNO}_3 = \text{AgNO}_3 + \text{H}_2\text{O} + \text{NO}_2$ .
- II.  $3 \text{Cu} + 8 \text{HNO}_3 = 3 \text{Cu}(\text{NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO}$ .
- III.  $\text{AgNO}_3 + 2 \text{KCN} = \text{KAg}(\text{CN})_2 + \text{KNO}_3$ .
- IV.  $2 \text{Cu}(\text{NO}_3)_2 + 4 \text{KCN} = 2 \text{Cu}(\text{CN})_2 + 4 \text{KNO}_3$ .
- V.  $2 \text{Cu}(\text{CN})_2 = (\text{CN})_2 + 2 \text{CuCN}$ .
- VI.  $2 \text{CuCN} + 6 \text{KCN} = 2 (\text{CuCN} \cdot 3 \text{KCN})$ .

\* This particular method has been selected because of its simplicity. The directions, which are for an alloy high in copper, may by slight modifications be used for the common alloy, coinage silver (see Fact 76).

† Smith and Frankel, J. A. C. S., 1890, p. 104; Smith and Spencer, J. A. C. S., 1894, p. 420; Smith and Fulweiler, J. A. C. S., 1901, p. 582; *Electro-Analysis*, Edgar F. Smith, 1907.

## DETERMINATION OF SILVER AND COPPER

## PROCEDURE \*

Weigh one portion of about 0.5 of a gram of silver-copper alloy<sup>76</sup> into a 250 c.c. casserole. Weighing the alloy  
Read Fact 77 and then dissolve the alloy in the least possible amount of *nitric acid* (1.4 sp. gr.). Dissolving the alloy

Evaporate to dryness on the water bath.

While this is on the water bath, clean with sapolio and then chromic acid the platinum electrode that is to be used as the cathode. Preparation of a cathode

Wash it with distilled water until it is thoroughly rinsed.

Hold it in the pincers and pass it through a flame till it is red hot.

Put it into a desiccator to cool.

---

EXPLANATORY FACTS

76. If coinage silver—ninety parts of silver to ten of copper—is used for this determination, use less KCN than in the above directions, allow more time for depositing the silver and less for depositing the copper. A quarter of a ten-cent piece weighs about 0.7 of a gram.

77. All excess of nitric acid *must* be removed in the next step by evaporation to dryness. KCN *must not* be added to an acid solution. It would evolve volatile HCN, which is a poison.

\* This process is given through the courtesy of Edgar F. Smith, Professor of Chemistry at the University of Pennsylvania. His experiments were made with an alloy of approximately ten parts of silver to ninety parts of copper.

When cool, weigh and note the weight.

When the above solution is evaporated to dryness, dissolve the residue in hot water.

Transfer the solution quantitatively to a 100 c.c. volumetric measuring flask.\*

Wash down the inside of the neck and add distilled water till the meniscus (see page 99) is exactly at the 100 c.c. line on the neck. Dry the inside walls of the neck above the line with a piece of filter paper rolled around a stirring rod.

Pour the solution back and forth into a perfectly dry beaker till it is thoroughly mixed. When not in use keep this measuring flask closely stoppered to prevent evaporation.

Measure with a 25 c.c. volumetric measuring flask or pipet<sup>78</sup> exactly 25 c.c. of the solution. This is an Measuring an aliquot part aliquot part, one-quarter of the solution.

Pour this aliquot part into a small dry beaker holding about 200 c.c. With distilled water wash out several times the 25 c.c. flask to be sure that the solution is quantitatively transferred.

Dilute to about 125 c.c.

Read Fact 79 and then, following precautions, add about 2 grams<sup>80</sup> of the potassium cyanid, KCN.†

---

#### EXPLANATORY FACTS

78. Aliquot parts, or definite fractions of the whole volume of a uniform solution, should be measured only in dry measuring dishes or in those which have been washed out with several small portions of the solutions to be measured.

79. Potassium cyanid is a *violent poison!* The student must handle it with the greatest care! He must wash his hands carefully after using it and at no time during this experiment should he drink from laboratory dishes.

80. The amount of KCN added varies according to the relative per cent. of the copper and silver. Use approximately 2 grams of KCN for each 0.1 of a gram of copper.

\* Read the paragraph on "Measuring Flasks," page 99.

† "Chemistry of the Metals," Experiments Nos. 49 and 104.

## DETERMINATION OF SILVER

With the aid of the instructor, attach the weighed cathode to the negative pole of the circuit and the anode to the positive pole.

Arrange the two electrodes about one centimeter apart in the solution. Do not let them touch the bottom of the beaker. Electrolytic  
deposition

Use a current density of approximately 2.5 volts and 0.06 to 0.1 of an ampere for 100 sq. cm. of cathode surface.<sup>81</sup>

Heat the solution to a temperature<sup>82</sup> of about 65° C.

Test with a thermometer but, to avoid loss when it is taken out, wash it off into the solution.

Switch on the electric current for the deposition of the silver and allow from two to three hours.

At the end of two hours one drop of the solution may be tested for silver. Test for complete  
deposition of silver

When there is no silver left in the solution and the deposition is therefore shown to be completed, have at hand bottles of alcohol and ether, a wash bottle and a piece of filter paper laid on a five-inch watch glass. The following work should be done expeditiously.

---

EXPLANATORY FACTS

81. Unless connections have been used in previous work and the terminals marked, it will be necessary to determine beforehand by experiment which is the negative pole. This can be done by the use of an ammeter upon which the poles are marked or by passing a current through a dilute copper sulfate solution in which there are two unweighed platinum electrodes. The copper is deposited on the negative electrode.

82. At a temperature of 65° C., 0.2 to 0.3 of a gram of silver may be precipitated in four hours. If the solution is cold, it will probably take ten hours for 0.2 of a gram to precipitate.

Lift the cathode from the solution.

Wash it thoroughly with a stream of water from the wash bottle, catching the washings in the beaker.<sup>83</sup>

Preparation of the cathode and silver deposit for weighing

Pour alcohol<sup>84</sup> completely over each side of the electrode.

Do the same with ether.

Place the cathode on the filter paper on the watch glass.

Put the watch glass in an air bath that is *not hotter* than 100° C., for a few moments only, until dry. Lest the cathode be forgotten, do nothing else until it is dry.

Place in a desiccator, cool and weigh. Note the weight.

After the final weight has been made, in a beaker dissolve the silver from the cathode with hot, dilute *nitric acid*.

Put this solution in the "silver residue" bottle. Wash the cathode, polish it with sapolio, clean it thoroughly, dry, ignite and weigh.

Leave it in the desiccator ready for the next deposition.

#### DETERMINATION OF COPPER

The silver has been removed but the solution still contains the copper which did not deposit at so low a current density. The potassium cyanid which was added at the start is still present. The best working volume under these conditions has been found to be 150 c.c.

This solution is probably, because of previous washings, about 150 c.c. If not, evaporate it to this volume.

---

#### EXPLANATORY FACTS

83. The solution that clings to the cathode contains some of the copper which is to be quantitatively determined.

84. Do not pour alcohol and ether near a flame. Allow "washings" to fall into a clean, dry beaker to be saved in "residue bottles."

## PROCEDURE

Add 10 c.c. of *ammonium hydroxid*,<sup>85</sup>  $\text{NH}_4\text{OH}$  (0.96 sp. gr.).

Arrange the electrodes as before.

Use a current density of approximately 5 volts and 1 ampere for 100 sq. cm.

Keep the temperature of the solution at 65° C.

At 65° C., about 0.2 of a gram of copper will be deposited in an hour.

Deposition of the  
copper

Two hours therefore should be allowed. At the end of this time, add a little distilled water to the solution to raise its level.

If no new copper appears on the fresh surface of the platinum, the deposition may be considered complete.

Lift the cathode from the solution and wash quickly and thoroughly with distilled water.

Wash with alcohol and with ether as before, save washings in the "residue bottles."

Preparation of the  
cathode and copper  
deposit for weighing

Place the cathode on a filter paper on a watch glass and put in an air bath not hotter than 100° C. till dry, but no longer.

Cool in a desiccator and weigh.

After the weight has been made, dissolve the copper from the cathode with dilute *nitric acid*.

Wash the cathode and as previously described prepare it for the check analysis.

---

EXPLANATORY FACT

85. In alkaline cyanid solution, there is a tendency for the platinum of the anode to be deposited with the copper on the cathode. If, however, the cyanid is not largely in excess, and if the current is interrupted as quickly as possible after the copper is deposited, this error is reduced to a minimum. It has been determined that in the presence of a definite amount of ammonium hydroxid there is absolutely no loss sustained by the anode in cyanid electrolyte and that the precipitation is much accelerated ("Electro-Analysis," Smith, page 71).

**Duplicate Analysis**

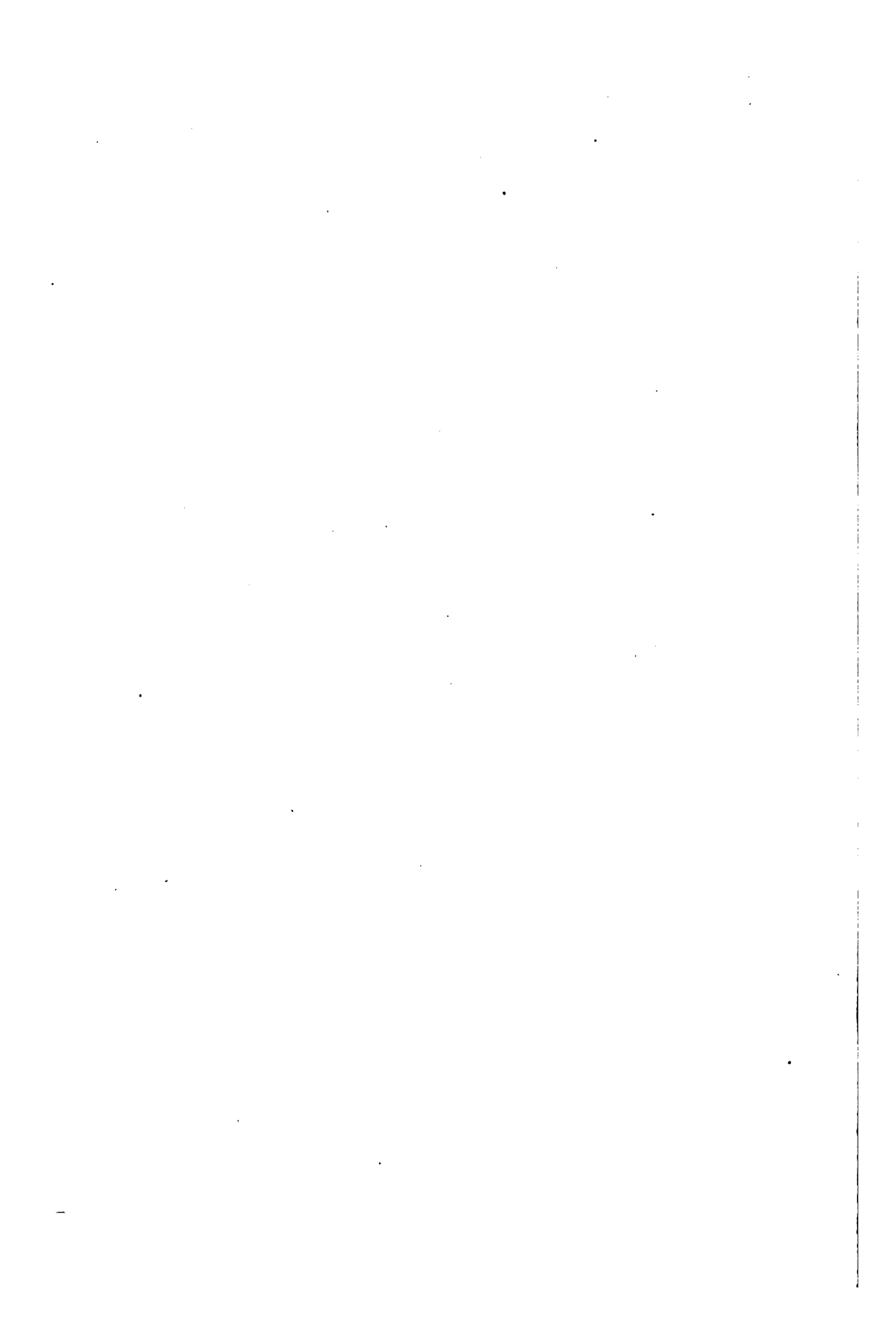
Use another aliquot part of 25 c.c. of the original solution and make a check analysis of both the silver and copper.



## SECTION III

---

### VOLUMETRIC ANALYSIS



## VOLUMETRIC ANALYSIS

---

### Comparison of Volumetric and Gravimetric Methods

IN *Gravimetric Analysis* the element or radical to be determined is either isolated or combined in an insoluble compound and weighed. This process of isolation or combination often requires a series of careful and prolonged operations. In *Volumetric Analysis* (1) the element or radical to be determined is not necessarily isolated but is often treated in the presence of the other constituents. To make this possible, the exact qualitative content should be known and all reactions that are likely to occur in the course of the analysis should be understood. (2) In the oftentimes greater simplicity of the processes involved, in the fewer weighings, and in the usual absence of much filtering and washing, the chance of error is less than in Gravimetric Analysis and (3) the saving of time, especially in a case of routine work which requires the analysis of many samples a day, is very great.

*Volumetric Analysis* is the quantitative determination of an element or radical in a substance, — a determination, as its name indicates, made by adding a volume of a selected solution sufficient to cause definite, complete reaction.

### Measuring Instruments

For the accurate measurement of liquids there are certain graduated glass vessels, the *pipet*, *measuring cylinder*, *measuring flask* and *buret*.

For the best results, it is most important that the measuring instruments be graduated accurately and that they agree among themselves.

In a longer course of Volumetric Analysis it is customary to have the students calibrate\* to verify the capacity of these instruments. In this short course, if possible, it would be well for the department to have the instruments calibrated and to issue calibration cards showing the variation of the instruments. If this is not possible the errors, which are often slight, may be ignored and a wider latitude allowed in the results obtained.

*Pipets* are used to measure exactly small amounts of solutions. They are either graduated to deliver a specified quantity, such as 10 c.c., 50 c.c., etc., or are graduated in fifths or tenths of a cubic centimeter to deliver any desired fractional part of the whole quantity. The pointed end of the pipet is dipped into the solution, the mouth is applied to the other end and the liquid sucked into the pipet up to the mark. The forefinger is placed over the top end to keep the solution from running out. The pressure of the finger regulates the flow from the pipet. In case of a "one-quantity" pipet, to insure complete delivery, the pipet should be inclined against the side of the dish and the last drop blown out. Pipets are graduated to *deliver* their contents; the mark is therefore high enough to include the liquid that adheres to

\* For methods of calibrating pipets, flasks, cylinders and burets, see Sutton's "Volumetric Analysis," pages 18-20.

the inside walls; in other words, it delivers into another receptacle the exact amount marked, but holds a trifle more. The point of a pipet should be sufficiently fine so that the liquid will not be delivered too quickly.

*Measuring flasks*, stoppered glass vessels with narrow necks, are graduated either to deliver or to contain or both, in which latter case the upper mark is that of delivery. Each measuring flask and pipet should have etched upon it its capacity, the temperature at which the graduation was made and the line that marks the limit of definite content. A specially constructed flask has along the length of the inside wall of its neck a broad blue line on a background of white enamel. This facilitates the reading by the reflection of the blue on the "*meniscus*"—the curved line of the surface of the liquid—which makes the blue line narrow into a point.

*Measuring cylinders*, glass cylinders of varying sizes, are graduated to deliver and are used for mixing and for making comparatively rough measurements.

*Burets*, graduated glass tubes of large bore, with cocks at the lower end for controlled delivery, are graduated in fifths, tenths or twentieths of a cubic centimeter and hold twenty-five, fifty or one hundred cubic centimeters. The two common forms of buret are the Geissler, or Fresenius, type with glass stopcock and the Mohr type with a rubber tip closed with a metal pinchcock or a glass ball acting as a valve. Burets are supported upon stands. One convenient model is the Chaddock, in which the burets are held by easily manipulated wire clips which prevent slipping and hold the buret firmly vertical. The white porcelain base serves as an excellent background against which end points are well determined.

### Reading the Instruments

The surface of liquids in narrow vessels is, because of capillary attraction, concave and, in the case of mercury, convex. This makes it necessary to select some point on the curved line to coincide with the graduation mark in the instrument. In the case of all light-colored liquids, it has been found advisable to select the lowest point of the concave line,—the bottom point of the “meniscus”; with dark or opaque liquids, the highest point on the extreme upper level.

Before reading any graduated instrument, its exact vertical position must be assured.

In reading a buret, the eye should be on a level with the selected point of the meniscus and its position in relation to the graduated lines on the buret noted.

If the student is not provided with a buret made with a longitudinal blue line on a white, enameled background, he may, with advantage, hold a piece of dark glazed paper at the back of the buret about one-eighth of an inch below the surface of the liquid. This will make the lower part of the meniscus appear as a well-defined black line against the white.

A buret reading should not be taken until all liquid which may cling to the walls of the buret has had time to flow into the main bulk of the liquid. Three minutes is the usual time allowed for the liquid to collect. A uniform rate of delivering the liquid should be adopted. After a rapid run it takes more time for the liquid to collect than after a slow run.

### General Directions

The perfect cleanliness of the volumetric measuring apparatus is essential. Grease, which makes the liquid gather in drops on the walls, may be removed with a dilute solution of sodium hydroxid, NaOH; or acidified potassium dichromate,  $K_2Cr_2O_7$ , or chromic acid,  $CrO_3$ .

Any volumetric instrument even if new and dry should be rinsed out with three successive small portions of the solution with which it is to be filled. It is absolutely necessary that all standard solutions should be kept at their known established strength, that they should not be diluted with any drops of water which may be adhering to the walls of the measuring vessels and that they should not be contaminated with any foreign matter.

In Volumetric Analysis to insure accurate results the conditions should be kept as uniform as possible, — conditions of intensity of light, temperature, time of waiting before taking readings, reading of tenths and end points. To practise the reading of tenths, the buret may be filled with water and, as it is allowed to escape drop by drop, the surface of the water, as the level is lowered, may be watched and its exact position noted in reference to the graduation lines. In this way, accurate reading of the tenths is easily mastered.

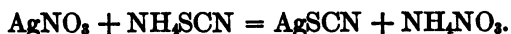
### Standard Solutions

A solution whose exact content per cubic centimeter has been determined is a *standard solution* and is said to have been *standardized*.

The process of adding a definite quantity of a standardized liquid to a solution to estimate its value or to a solution of a substance to be analyzed is called *titration*.

An acid solution, for instance, is standardized and alkali titrated with it to estimate the value of the alkali in terms of the acid and *vice versa*. A solution of a salt is standardized to be used for the oxidation, reduction or precipitation of the solution to be analyzed.

A solution of known composition and standard strength is used to cause a complete, definite reaction with a solution of the substance to be analyzed. For example, a solution of ammonium sulfo-cyanid whose exact strength is known is added to a solution of silver nitrate to be analyzed. These react as follows:



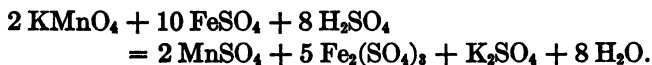
When the silver in the silver nitrate is entirely changed to sulfo-cyanid, another drop of the ammonium sulfo-cyanid will form no further precipitate (see under "End Point" 2, b). The strength of the ammonium sulfo-cyanid is known and also the exact amount in cubic centimeters that it took to precipitate the silver. From this data and the relation of the molecular weights the amount of silver present in the silver nitrate can be calculated.



### End Point

The exact point at which such reactions are complete is called the *end point*. The end point is shown:

1. By the persistence of the color of the standard solution used. This shows the completion of chemical action. Thus: A solution of ferrous sulfate is titrated with a standardized solution of potassium permanganate in the presence of sulfuric acid,

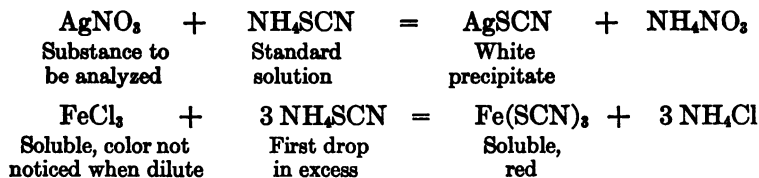


The color of the standard solution,  $\text{KMnO}_4$ , is pink. Just as long as any of the ferrous sulfate is left, the potassium permanganate continues to decompose and to lose its pink color. When the reaction is completed, the permanganate is no longer decomposed and its pink color persists.

2. By the formation of, or change in, the color of a substance, called an *indicator*, originally added for this purpose to the solution to be analyzed. Thus:

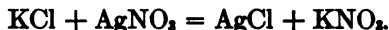
a. With an organic indicator, such as methyl orange, in the presence of alkalies its red color changes to yellow or, again, colorless phenolphthalein in the presence of alkalies turns bright red.

b. With an inorganic indicator, such as ferric chlorid in the following illustration, after the main reaction is completed, the soluble, red  $\text{Fe}(\text{SCN})_3$ , is formed.

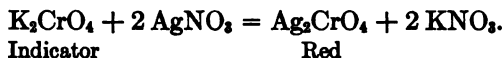


3. By the formation of a precipitate. Thus: A standardized solution of silver nitrate is added to a solution of potassium

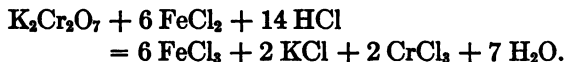
chlorid to be analyzed, in which there is an indicator, potassium chromate.



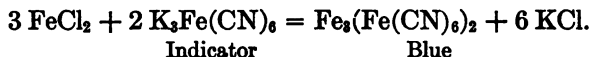
When all of the potassium chlorid has been used to form white silver chlorid, the next drop of the reagent, silver nitrate, reacts with the potassium dichromate to form silver chromate which is red.



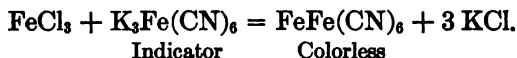
4. By the failure to produce color when a drop of the solution being analyzed is added to an indicator in a separate container. Thus: A standardized solution of potassium dichromate is added to a solution of ferrous chlorid to be analyzed in the presence of hydrochloric acid,



The indicator, potassium ferricyanid, is in a separate dish. If, *before* the reaction is completed, a stirring rod is dipped into the above solution and then into the indicator, there is formed a blue precipitate, according to the equation,



When the ferrous chlorid is all oxidized to ferric chlorid and a drop of the solution is added to the indicator, there will be no color, according to the equation,



### Indicators

Indicators as illustrated above are used to show, by color changes or by a precipitation, a condition of acidity, alkalinity, neutrality or, in general, the completion of reaction. They may be (1) dye-stuffs; (2) the coloring matters of plants, which are generally weak acids; salts of weak acids or, less often, weak bases; or (3) inorganic compounds which form a coloration or a colored precipitate at the end of a reaction.

An indicator must take no part in the reaction going on but as the reagent is added must itself remain inert till the main reaction is completed. After the completion of the reaction, the next drop of the liquid acts on the indicator in the solution and gives ocular evidence that the end point has been reached. There is no one indicator that can be universally used. That which answers for one analysis may be useless for another. Its value depends upon the sensitivity of its action and upon the sharpness and intensity of the color it affords.

Indicators have been divided by R. T. Thomson\* into three classes: (1) Those capable of forming *stable* salts, as methyl orange. These are most sensitive to alkalies. (2) Those forming unstable salts which hydrolyze in water, as phenolphthalein. These are most sensitive to acids. (3) Those midway between the two, as litmus. These are fairly sensitive to both alkalies and acids.

The theories of the action of indicators are by no means final. According to Ostwald, an indicator, for at least acids and bases, must possess a color when undissociated different from that which it has when ionized.† That is, the color changes are ascribed to the dissociation and caused by the addition of a substance to the indicator. It is, therefore, the color reaction caused by the hydrogen or hydroxyl ions of dissociated acids or bases which makes some dyes of service as indicators.

\* J. S. C. I., volume 6, 1887, page 195.

† Ostwald's "Lehrbuch der Allgemeinen Chemie."

Strong acids and strong bases, since they ionize readily, are not useful as indicators. Weak acids and weak bases are more or less undissociated in solution and are ionized only after conversion to a neutral salt.

This will be made clear by the following examples:

(a) Phenolphthalein, — belonging to class 2, — a weakly acid indicator, is undissociated and colorless in acid solution. Its alkali salt is, however, at once dissociated and the red color of the ion at once shows the completion of the neutralization of the solution.

(b) Methyl Orange, — belonging to class 1, — a moderately strong acid indicator, is undissociated and of a pinkish red color in acid solution. When an acid solution containing the indicator methyl orange is titrated with a solution of an alkali, the first drop of alkali after the end point has been reached forms a salt with the methyl orange. The salts of methyl orange are readily dissociated, whereupon the red of the nonionized indicator changes to yellow, the color of the ion.\*

The following are but a few of the indicators in general use: litmus, methyl orange, phenolphthalein and lacmoid.

#### Litmus

With acids.....red.

With alkalies.....blue.

This is a violet-blue, organic pigment sensitive to both acids and alkalies. It cannot be used with bicarbonates and carbonates, as the liberated carbonic anhydrid dissolves and causes the red color to persist even if the liquid is alkaline. It can, however, be used if the solution is boiling, as this gas is then constantly evolved.

#### Methyl Orange

With acids.....pinkish red.

With alkalies.....yellow.

This is the sodium or ammonium salt of a specific organic acid, synthetically prepared. It is an ochre yellow powder which when

\* For further study of this subject, the student is referred to such textbooks as: Jones's "Theory of Electrolytic Dissociation" and Cohn's "Indicators and Test Papers," from which some of the above statements are taken.

dissolved in water forms a yellow solution. Methyl Orange is particularly sensitive to alkalies. An excess of this indicator should be avoided, as the color changes are then not so sharp. The yellow color is not affected by alkalies or by carbonates of the alkalies, but is changed to a pinkish red by acids, becoming yellowish red on approaching neutralization.

Carbonic, boric, silicic, arsenious and some organic acids, including some of the fatty acids, do not cause methyl orange to change to red.

#### Phenolphthalein

With acids.....colorless.

With alkalies.....red.

This is an organic compound synthetically prepared. It is a cream-white, crystalline powder. Phenolphthalein has the properties of a very weak acid and is extremely sensitive. Even carbonic acid causes a change. Titrations, therefore, in the presence of carbonates, can be done only in boiling solution. One part of alkali in 100,000 parts of water will give a distinct color. It cannot be used in the presence of ammonium salts.

#### Lacmoid

With acids.....red.

With alkalies.....violet blue.

This is another organic compound synthetically prepared. It is in the form of blue-black scales. Lacmoid is sensitive to both acids and alkalies. It can be used in the presence of carbonates only in hot solution.

### Normal Solutions

A normal solution ( $\frac{N}{1}$ ) is one that contains in one liter as many grams of the active substance as its molecular weight divided either by its replaceable hydrogen atoms or the equivalent of such hydrogen atoms.

(A) Reagents with replaceable hydrogen atoms, such as HCl, H<sub>2</sub>SO<sub>4</sub>.

1. The molecular weight of HCl = 36.45. This expressed in grams is 36.45 grams. HCl has one replaceable hydrogen atom; therefore,  $36.45 \div 1 = 36.45$ , the weight required.

*A normal solution of HCl contains in one liter 36.45 grams of HCl.*

2. The molecular weight of H<sub>2</sub>SO<sub>4</sub> = 98.07. This expressed in grams is 98.07 grams. H<sub>2</sub>SO<sub>4</sub> has two replaceable hydrogen atoms; therefore,  $98.07 \div 2 = 49.03$ , the weight required.

*A normal solution of H<sub>2</sub>SO<sub>4</sub> contains in one liter 49.03 grams of H<sub>2</sub>SO<sub>4</sub>.*

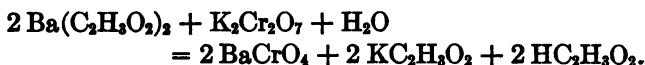
(B) Reagents containing no replaceable hydrogen atoms, such as NaOH, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and SnCl<sub>2</sub>.

3. The molecular weight of NaOH is 40.058. This expressed in grams is 40.058 grams. Na is monovalent and therefore equivalent to one atom of replaceable hydrogen.

*A normal solution of NaOH, therefore, contains in one liter 40.058 grams of NaOH.*

The equivalent of the replaceable hydrogen atoms differs according to the reaction that is to take place. Potassium dichromate, for example, can be used either as a precipitating or as an oxidizing agent.

4. As a precipitating agent, potassium dichromate reacts as follows:



In this reaction, for every molecule of the reagent  $\text{K}_2\text{Cr}_2\text{O}_7$ , two molecules of  $\text{BaCrO}_4$  are precipitated, which require two atoms of Ba in the two molecules of  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ . Each atom of Ba is equivalent to two of H, therefore the two atoms of Ba used in this precipitation are equivalent to four atoms of hydrogen.

In a normal solution of potassium dichromate used as a precipitant, then, its equivalent in replaceable hydrogen atoms is four.

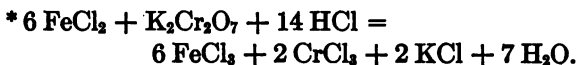
The molecular weight of  $\text{K}_2\text{Cr}_2\text{O}_7 = 294.5$ .

This expressed in grams is 294.5 grams.

$$294.5 \div 4 = 73.62.$$

*A normal solution of potassium dichromate used as a precipitant contains in one liter 73.62 grams.*

5. As an oxidizing agent, potassium dichromate reacts as follows:



In this process of oxidation,  $\text{K}_2\text{Cr}_2\text{O}_7$  acts as if it split up into  $\text{K}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{O}_3$ . Each molecule of  $\text{K}_2\text{Cr}_2\text{O}_7$  frees three atoms of O for oxidizing purposes. In the above reaction, for three atoms of O liberated in a molecule of the reagent  $\text{K}_2\text{Cr}_2\text{O}_7$ , there are six atoms of chlorine liberated to combine with the ferrous chlorid to form ferric chlorid. Six atoms of Cl are equivalent to six atoms of H.

\* "Chemistry of the Metals," Experiment No. 200.

In a normal solution of potassium dichromate used as an oxidizing agent, its equivalent in replaceable hydrogen atoms is six.

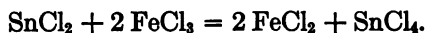
The molecular weight of  $K_2Cr_2O_7 = 294.5$ .

This expressed in grams = 294.5 grams.

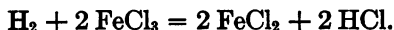
$294.5 \text{ grams} \div 6 = 49.08 \text{ grams}$ .

*A normal solution of potassium dichromate used as an oxidizing agent contains in one liter 49.08 grams, one-sixth of its molecular weight in grams.*

6. As a reducing agent stannous chlorid reacts as follows:



In this reaction, every molecule of the reagent,  $SnCl_2$ , reduces two molecules of the ferric chlorid ( $2 FeCl_3$ ) to two molecules of ferrous chlorid ( $2 FeCl_2$ ). Each molecule of the  $SnCl_2$ , then, removes two atoms of chlorin which are the equivalent of two atoms of hydrogen. This may also be shown by the reaction



*In a normal solution of stannous chlorid used as a reducing agent, its equivalent in hydrogen atoms is two.*

The molecular weight of  $SnCl_2 = 189.90$ .

This number expressed in grams = 189.90 grams.

$189.90 \div 2 = 94.95 \text{ grams}$ .

*A normal solution of the reducing agent stannous chlorid contains in one liter 94.95 grams of  $SnCl_2$ , one-half of its molecular weight in grams.*

A solution of one-half the strength of a normal solution is called a *seminormal solution*  $\left(\frac{N}{2}\right)$ .

A solution of one tenth of the strength of a normal solution is called a *decinormal solution*  $\left(\frac{N}{10}\right)$ , etc.



### Permanency of Standard Solutions

Solutions of the nature of those just described do not remain of the same strength for an indefinite period of time. Evaporation and chemical changes, including those resulting from the action of light, and action upon the glass of the bottle all contribute to render a standardization accurate for a comparatively limited time only. Thus, silver nitrate is reduced in the light and silver is deposited, weakening the solution; potassium permanganate deposits oxids of manganese, and sodium hydroxid reacts with the glass of the bottle. Even at normal temperature, a solution of any substance evaporates and the solvent condenses on the sides of the bottle or, if imperfectly corked, it escapes into the air. It is therefore necessary to keep the bottle carefully stoppered, to keep it in a cool dark place and to shake it thoroughly in order to wash down its inner wall before using. It is also advisable not to make up too large a quantity of solution of a substance that acts upon the glass. Any solution about whose exact strength there is any doubt should be restandardized.

### Acidimetry and Alkalimetry

The processes of Acidimetry and Alkalimetry are those by which the strength of acids and bases are determined.

#### STEPS TO BE CONSIDERED IN PREPARING AND STANDARDIZING HALF-NORMAL SOLUTIONS OF HYDROCHLORIC ACID AND SODIUM HYDROXID

- (1) Preparation of an approximately half-normal solution of hydrochloric acid.
- (2) Preparation of an approximately half-normal solution of sodium hydroxid.
- (3) The titration of the acid against the alkali for the determination of the *relative* values of the approximately half-normal solutions of hydrochloric acid and sodium hydroxid.
- (4) The use, through factors, of *approximately* half-normal solutions as standard solutions.
- (5) The determination with Iceland spar or pure sodium carbonate of the *absolute* value of the approximately half-normal solution of hydrochloric acid and the preparation of an *exactly* half-normal solution of hydrochloric acid.
- (6) The preparation of an *exactly* half-normal solution of sodium hydroxid by use of the *previously established values*.
- (7) The determination with oxalic acid of the absolute value of the approximately half-normal solution of sodium hydroxid and the preparation of an *exactly* half-normal solution of sodium hydroxid.
- (8) The reestablishment of the relative values of the two solutions, which, if correctly diluted, should now be equal, volume for volume.

(1) *Preparation of an Approximately Half-Normal Solution of Hydrochloric Acid*

Theoretically the simplest way to prepare accurate standard solutions is to dissolve calculated and carefully measured amounts of substances in an exact amount of solvent. As a matter of fact, however, neither the conditions nor the chemicals used in most cases are sufficiently to be relied upon to give perfect results.

An approximately normal solution can be made and its relative value to an exactly normal solution can be determined or an exactly normal solution can be prepared from the one that is approximately normal.

CALCULATION OF THE NUMBER OF CUBIC CENTIMETERS OF  
AQUEOUS HYDROCHLORIC ACID REQUIRED TO MAKE A  
LITER OF A HALF-NORMAL SOLUTION

As a solution of hydrochloric acid gas is to be used, it is necessary to calculate the *weight* of the hydrochloric acid gas contained in the *aqueous* hydrochloric acid.

A normal solution of HCl should contain 36.458 grams of HCl gas in one liter.

At 15° C., HCl (sp. gr. 1.2) contains 39.1% of HCl by weight.

In 100 c.c. of aqueous HCl (sp. gr. 1.2) there are 46.92 grams of HCl gas for:

$$100 \text{ c.c.}$$

$$\underline{1.2}$$

$$120 \text{ grams} = \text{weight of 100 c.c. of aqueous HCl.}$$

$$.391 \times 120 \text{ grams} = 46.920 \text{ grams.}$$

$$46.92 \text{ grams} = \text{weight of HCl gas in 100 c.c. of aqueous HCl.}$$

To furnish 36.458 grams of HCl gas, there must be 77.70 c.c. of aqueous hydrochloric acid (sp. gr. 1.2) according to the following proportion:

$$46.92 : 36.458 :: 100 : x$$

$$x = 77.70 \text{ c.c.}$$

In a liter of a normal solution of hydrochloric acid,  $\frac{N}{1}$ , then, there are 77.7 c.c. of aqueous hydrochloric acid (sp. gr. 1.2).

In a half-normal solution,  $\frac{N}{2}$ , there are in every liter one-half of 77.7 c.c. or 38.85 c.c. of aqueous HCl (sp. gr. 1.2) measured at 15° C.

---

#### PROCEDURE

In a graduated cylinder measure a volume approximately equal to 38.8 c.c. of *aqueous hydrochloric acid* (sp. gr. 1.2) and about one-tenth as much in addition.<sup>86</sup>

Add enough distilled water to dilute to one liter and shake<sup>87</sup> for a minute or more. If the cylinder is too full to allow the liquid to be shaken thoroughly, transfer to a beaker, stir vigorously and return the solution to the bottle.

Preparation of the  
standard acid solu-  
tion

Label the bottle "Approximately  $\frac{N}{2}$  HCl".

---

#### EXPLANATORY FACTS

86. The extra volume is added to make sure that it is stronger than half-normal. It is easier later to dilute than to add an exact amount of acid.

87. It is of the utmost importance to get the solution into a homogeneous state.

N. S. 11

(2) *Preparation of an Approximately Half-Normal Solution of Sodium Hydroxid*<sup>88</sup>

PROCEDURE

Calculate in the notebook the amount of *caustic soda*, NaOH, necessary to make one liter of a half-normal solution.

Weigh<sup>89</sup> out on a rough balance in a counterbalanced porcelain dish an amount equal to the calculated weight plus one-tenth as much in addition.<sup>90</sup>

Measure 1000 c.c. of distilled water in a measuring cylinder.

Dissolve the *sodium hydroxid* in a part of this distilled water *contained in a beaker or* Preparation of the standard alkali solution *porcelain dish.*

Stir until the hydroxid is all dissolved and then cover with a watch glass till it is somewhat cooled.

Transfer the solution to a bottle, add the rest of the distilled water and shake vigorously.

Label the bottle, which must have a rubber stopper or a glass stopper *lightly* covered with vaseline, —

“Approximately  $\frac{N}{2}$  NaOH”.

---

EXPLANATORY FACTS

88. Standard acid solutions may be kept for some time without deterioration. This is not the case with standard alkali solutions which absorb carbon dioxid from the air and, as has been said, act upon the glass of the bottles in which they are contained. It is therefore important to titrate the alkali frequently with a standard acid in order to reestablish its strength.

89. Weigh quickly and do not leave exposed to the air, as caustic soda is hygroscopic. Cork the stock bottle *at once*.

90. Sodium hydroxid, caustic soda, is an excellent alkali for general use; it is a strong base, forms soluble salts with all acids and, being readily soluble (133.3 parts in 100 parts of water), may be made up to a strong solution.

*(3) The Titration of the Acid against the Alkali  
and  
The Calculation of the Relative Values of the Approximately  
Half-Normal Solutions of Hydrochloric  
Acid and Sodium Hydroxid*

PROCEDURE

Wash two burets thoroughly with distilled water. When they are emptied, no drops should adhere to the inner walls. If they do, the surface is not clean and should be treated with "chromic acid mixture."

Put a label on the top front of each buret, one Labeling the  
burets marked "HCl" and the other "NaOH".

Fit a cork to each and label each cork, one marked "HCl" the other "NaOH". Keep a small, properly labeled watch glass upon which to lay each cork.

Close the outlet of the "HCl" buret and Filling the burets pour in 5 c.c. of the again well-shaken  $\frac{N}{2}$  HCl.

Hold the stoppered buret in a nearly horizontal position and allow the acid to flow over the entire interior and shake. Then remove the cork and let the acid run out through the outlet.

This should be repeated.

Treat the "NaOH" buret in the same way. (If it is certain that the burets are absolutely dry, the foregoing may be omitted.)

Put a small glass funnel into the top of each buret with the stem against the inner wall and fill each buret with its well-shaken solution.

Let enough of each liquid run through the tips to insure the removal of any air bubbles.

If there are any drops of the liquid left on the inner walls of the burets above the zero mark, absorb with a filter paper rolled around a glass rod.

Be sure that the burets are perfectly vertical.

Run out the liquid in each buret till the bottom of the meniscus stands at the zero mark. If a "blue line" buret is used, bring the constriction seen on the blue line to the zero mark.

If the liquid is below the zero mark, make a careful reading at such a point.

Record the reading in the notebook. It is well to keep the HCl and NaOH readings in the same relative positions on the page as the positions of the burets (see next page).

Run about 40 c.c. of the *acid* into a casserole, an Erlenmeyer or an ordinary flask, containing about 40 c.c. of distilled water, and add two or three drops of *methyl orange indicator*. To mix well, stir with a rod or shake the flask with a rotary motion. Titration process

Include any drop hanging from the tip of the buret by touching it with the rod or with the inside of the neck of the flask and washing it down with water from a wash bottle.

Run into the container about 5 c.c. less of the *sodium hydroxid* than that used of the hydrochloric acid and then slowly continue to add the sodium hydroxid solution, drop by drop, till the pinkish red solution turns yellow. Again do not neglect any hanging drops of the solution. Wash down the sides of the dish with distilled water.

Place the container under the HCl buret and continue to change from one buret to the other till one drop of the HCl or one drop of the NaOH changes the color.

As the pink is the sharper of the two color reactions, finish by adding a drop of HCl.

After a few minutes' wait for it to drain, note the reading of the HCl buret.

Continuing this, make six successive readings of these repeated changes and record as follows:

Readings. HCl	Actual number of c.c. used. 41.83 1.34 40.49	Relative Values.	Actual number of c.c. used. 39.1 0.5 38.6	Readings. NaOH
level at start, 1.34				level at start, 0.5
c.c.	c.c.		c.c.	c.c.
41.83	40.49	1.048	38.6	39.1
41.98	40.64	1.048	38.75	39.25
42.15	40.81	1.048	38.93	39.43
42.29	40.95	1.047	39.08	39.58
42.49	41.15	1.047	39.27	39.77
42.69	41.35	1.047	39.45	39.95
		Average 1.0475		

Therefore 1 c.c. of NaOH solution is equivalent to 1.0475 c.c. of HCl solution.

Shake the bottles containing the half-normal solutions, refill the burets and repeat the titration.

These results should check within 0.2 per cent. of the whole ratio.



(4) *The Use — Through Factors — of Approximately Half-Normal Solutions as Standard Solutions.*

Those limited in time need not prepare the *exactly* half-normal solutions, since the value of, or the degree of normality of, the approximately half-normal solutions may be determined by calculation.

It is, however, oftentimes desirable to have exact solutions.

Thus, as shown in the accompanying sample calculation (see page 126), 38.24 c.c. of *exactly*  $\frac{N}{2}$  HCl dissolves 0.9567 gram of  $\text{CaCO}_3$  whereas this same weight of  $\text{CaCO}_3$  dissolved in 34.49 c.c. of this particular solution of HCl.

The *approximately*  $\frac{N}{2}$  solution of HCl is therefore  $\frac{38.24}{34.49} = 1.108$  times stronger than semi-normal, *the factor of normality for the approximately  $\frac{N}{2}$  HCl solution.*

A given number of cubic centimeters of an *exact*  $\frac{N}{2}$  NaOH solution is exactly equivalent to the same number of cubic centimeters of an *exact*  $\frac{N}{2}$  HCl solution. But in establishing the absolute value of the HCl solution (see sample calculation p. 125) it was found that 40.0 c.c. approximately  $\frac{N}{2}$  NaOH solution neutralized 43.65 c.c. of approximately  $\frac{N}{2}$  HCl solution.

By using the factor of normality of this HCl solution, found above

to be 1.108, it is shown that 43.65 c.c. of this *approximately*  $\frac{N}{2}$  HCl is equivalent to 48.36 c.c. of *exact*  $\frac{N}{2}$  HCl solution.

$\therefore \frac{48.36}{40} = 1.209$ , the factor of normality for the *approximately*  $\frac{N}{2}$  NaOH solution.

The amount of *approximately* half-normal solution used can always be expressed in terms of the *exactly* half-normal solution by multiplying the number of cubic centimeters used by the factor of its normality.

If a solution is not exactly normal, the factor of its normality should be written on the label.

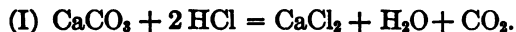
*(5) The Determination with Iceland Spar\* of the Absolute Value of the Approximately Half-Normal Solution of Hydrochloric Acid*

*and*

*The Preparation of an Exactly Half-Normal Solution of Hydrochloric Acid*

- (a) The solution of the Iceland spar,  $\text{CaCO}_3$ , in an excess of the approximately half-normal solution of hydrochloric acid.
- (b) The titrating back of the excess of acid with the approximately half-normal solution of sodium hydroxid.
- (c) The addition of the calculated amount of distilled water to the approximately half-normal solution of hydrochloric acid.

REACTIONS



\* If their purity and value is guaranteed, sodium carbonate or precipitated calcium carbonate may be used instead of Iceland spar.

### THE DETERMINATION OF THE ABSOLUTE VALUE

Pure calcium carbonate (Iceland spar) requires, of course, an exact amount of hydrochloric acid to dissolve it. The acid can therefore be standardized against it.

#### PROCEDURE

Weigh into Erlenmeyer or ordinary flasks<sup>91</sup> two portions of about 0.5 of a gram each of Iceland spar that has been ground to an impalpable powder.<sup>92</sup>

Weighing and dissolving the Iceland spar in a definite volume of hydrochloric acid

Add about 30 c.c. of the  $\frac{N}{2}$  HCl from the buret, make a note of the exact amount added.

Let this stand till the Iceland spar is wholly dissolved. Hold to the light to see if there are any particles undissolved. (While the Iceland spar is dissolving, begin to grind the iron ore according to the directions under "The Volumetric Determination of Iron in an Ore," page 150.)

---

#### EXPLANATORY FACTS

91. If dissolved in a flask, loss by effervescence is avoided. If, however, it is necessary to use a beaker, keep it covered. As the  $\text{CaCO}_3$  is somewhat slow to dissolve, full-strength acid solution acts as a better solvent.

92. Gritty particles dissolve slowly and with difficulty. Failure to dissolve completely the Iceland spar will result in error and will ruin subsequent analyses.

Add two or three drops of the *methyl orange indicator* and wash down the inside of the flask with water from a wash bottle. Make the initial reading on the NaOH buret and run in the NaOH till the indicator shows that the so- Titrating back the excess of acid lution has just become alkaline.

Again note the NaOH reading.

In case there is any doubt as to whether the exact end point was reached, titrate back with the hydrochloric acid and proceed to get an exact end point with the sodium hydroxid.<sup>93</sup>

Make careful readings.

Calculate the excess of acid which was used and then the amount of acid which combined with the calcium carbonate. This gives the amount of *approximately*  $\frac{N}{2}$  HCl necessary for this reaction. Calculate the theoretical amount of *exactly*  $\frac{N}{2}$  HCl necessary for this reaction. A comparison of these figures shows how much the *approximately*  $\frac{N}{2}$  HCl needs diluting to make it *exactly*  $\frac{N}{2}$ .

If the student's time admits of the standardization of the  $\frac{N}{2}$  solution of NaOH against oxalic acid, this standardization must be done *before* the *approximately*  $\frac{N}{2}$  solution of HCl is diluted to exactly  $\frac{N}{2}$  and while the relative values of the acid and alkali

---

#### EXPLANATORY FACT

93. A certain number of the cubic centimeters of the acid have been used in reacting with the calcium carbonate. The excess of acid above this amount has now been determined by titrating back with  $\frac{N}{2}$  NaOH solution.

solutions are still known. In which case, the acid may be diluted to exactly  $\frac{N}{2}$  *after* the standardization of the *approximately*  $\frac{N}{2}$  NaOH against oxalic acid. Otherwise, proceed with the dilution at this point (Calculation, page 127).

---

#### THE PREPARATION OF THE EXACTLY HALF-NORMAL SOLUTION

Measure accurately the amount of water to be added to the number of cubic centimeters of standard solution measured.

Add this exact amount from a graduated flask, pipet or buret.

Shake the solution till thoroughly homogeneous.

Dilution of the approximately  $\frac{N}{2}$  HCl solution to make an exactly  $\frac{N}{2}$  solution

## SAMPLE CALCULATIONS

FOR THE DETERMINATION OF THE ABSOLUTE VALUE  
AND OF  
THE QUANTITIES TO MAKE AN EXACTLY  $\frac{N}{2}$  SOLUTION OF HCl

If it takes 40 c.c. of an approximately  $\frac{N}{2}$  NaOH solution to neutralize 43.65 c.c. of an approximately  $\frac{N}{2}$  HCl solution, then 1 c.c. of  $\frac{N}{2}$  NaOH =  $\frac{43.65}{40}$  or 1.091 c.c. of  $\frac{N}{2}$  HCl ("Relative Value" of the two solutions).

Amount of  $\frac{N}{2}$  HCl added to the Iceland Spar = 45.40 c.c.

Amount of  $\frac{N}{2}$  NaOH used to titrate excess of acid = 10.00 c.c.

10.00 c.c. of this *approximate*  $\frac{N}{2}$  NaOH = 10.91 c.c. in terms of this *approximate*  $\frac{N}{2}$  HCl.

10.91 c.c. of HCl was neutralized by NaOH.

45.40 c.c.

10.91 c.c.

Therefore 34.49 c.c. were used to dissolve the Iceland Spar.

## ABSOLUTE VALUE

0.9567 g.  $\text{CaCO}_3$  required for solution 34.49 c.c.  $\frac{N}{2}$  HCl.



$$100.07 (\text{CaCO}_3) : 72.9 (2 \text{HCl}) = 0.9567 : x$$

$$x = 0.6969 \text{ gram of HCl.}$$

That is, 34.49 c.c. contain 0.6969 gram of HCl and therefore  
1 c.c. contains 0.0202 gram.

QUANTITIES TO MAKE AN EXACTLY  $\frac{N}{2}$  SOLUTION

34.49 c.c. of the approximately  $\frac{N}{2}$  HCl solution are needed to dissolve 0.9567 gram of  $\text{CaCO}_3$ .

How many cubic centimeters of an *exact*  $\frac{N}{2}$  solution would it take?

The equation in the foregoing section shows that it takes two molecules of HCl to dissolve one molecule of  $\text{CaCO}_3$ .

Molecular weight of  $\text{CaCO}_3 = 100.07$ .

One-half the molecular weight in grams = 50.035.

With a normal solution of HCl, a liter (1000 c.c.) is equivalent to 50.035 grams of calcium carbonate, therefore a liter of half-normal HCl is equivalent to 25.017 grams.

$$25.017 : 1000 :: 0.9567 : x$$

$$25.017 x = 956.70$$

$$x = 38.24$$

It takes, then 38.24 c.c. of an exactly  $\frac{N}{2}$  HCl solution to dissolve 0.9567 gram of calcium carbonate.



Since it took less of the *approximately*  $\frac{N}{2}$  HCl solution than it would have taken were the solution *exactly* half normal, it is too strong.

$$\begin{array}{r} 38.24 \\ 34.49 \\ \hline 3.75 \end{array}$$

Every 34.49 c.c. of the *approximately*  $\frac{N}{2}$  HCl should be diluted with 3.75 c.c. of distilled water to make it exactly semi-normal. If there are 500 c.c. of the *approximately*  $\frac{N}{2}$  HCl,  $\frac{500}{34.49} \times 3.75 = 54.3$  c.c. which is the number of cubic centimeters of water to be added to make the HCl solution exactly half-normal.

Fractional volumes should be measured with a buret. Measurements may be made by using a measuring flask nearest in size to the volume required and the rest of the volume added from a buret. By filling them as many times as necessary, burets only may be used.

(6) *The Preparation of Exactly Half-Normal Solution of NaOH from Previously Established Values*

If time is limited, the amount of water required to be added to the approximately half-normal solution of NaOH to make it *exactly* half-normal can be calculated from the data already obtained as follows:

Dilution of the approximately  $\frac{N}{2}$  NaOH solution to make an exactly  $\frac{N}{2}$  solution

$$1 \text{ c.c. } \frac{N}{2} \text{ NaOH was found to equal } 1.091 \text{ c.c. } \frac{N}{2} \text{ HCl.}$$

If 34.49 c.c. of *approximately*  $\frac{N}{2}$  HCl are diluted with 3.75 c.c. of distilled water to make an exactly  $\frac{N}{2}$  solution of HCl. then  $\frac{34.49}{1.091} = 31.61$  and  $\frac{3.75}{1.091} = 3.43$  c.c.

Therefore, in this case, every 31.61 c.c. of approximately  $\frac{N}{2}$  NaOH should be diluted with 3.43 c.c. of distilled water to make an exactly  $\frac{N}{2}$  solution of NaOH, or, to each cubic centimeter of the remaining solution, add 0.108 of a cubic centimeter of water.

#### PROCEDURE

Dilute the alkali as described under the directions for dilution of the acid.

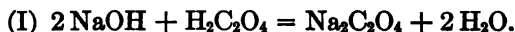
(7) *The Determination of the Absolute Value of the Approximately Half-Normal Solution of Sodium Hydroxid with Oxalic Acid*

*and*

*The Preparation of an exactly Half-Normal Solution of Sodium Hydroxid*

- (a) The titration of a solution of oxalic acid with the *approximately* half-normal solution of sodium hydroxid.
- (b) Titration back, with the *approximately* half-normal solution of hydrochloric acid, of the excess of alkali added.
- (c) Calculation and addition of the necessary amount of distilled water to the *approximately* half-normal solution of sodium hydroxid.

REACTIONS



## THE DETERMINATION OF THE ABSOLUTE VALUE

## PROCEDURE

Weigh into two casseroles two portions of pure, crystallized *oxalic acid*<sup>94</sup> ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ ) of about 0.8 gram each.

Dissolve in about 50 c.c. of water.

Heat to boiling and add a few drops of *phenolphthalein* indicator.

Titrate hot with  $\frac{N}{2}$  NaOH solution till it produces a pink color which lasts for a few minutes. Titration of the  
oxalic acid

Add from a half to one cubic centimeter of the  $\frac{N}{2}$  HCl solution noting the readings.

Bring to a boil.

---

EXPLANATORY FACT

94. If oxalic acid of this exact composition is not available, it may be prepared by Winkler's method ("Uebungen in der Massanalyse," p. 69). 500 grams of oxalic acid are dissolved in 500 grams of boiling HCl (1.07 sp. gr.). It is then allowed to crystallize by stirring the solution in a dish placed in ice water. The crystals are filtered through glass wool and washed with HCl. The yield is then redissolved in boiling hydrochloric acid, crystallized and filtered as before. This time, however, the crystals are washed with a little water and redissolved in just enough boiling water. The crystals obtained by cooling this solution are filtered and washed with water and recrystallized at least twice. The final crystals are then dried over a desiccating agent which must be frequently changed. It is now free from chlorin and mineral matter.

Titrate back with the  $\frac{N}{2}$  NaOH solution.

Calculate the excess of alkali added and then the amount of alkali which combined with the oxalic acid. This gives the amount of the *approximately*  $\frac{N}{2}$  NaOH solution necessary for this reaction.

---

#### THE PREPARATION OF AN EXACTLY HALF-NORMAL SOLUTION OF SODIUM HYDROXID

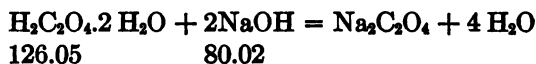
##### PROCEDURE

Calculate the amount of *exactly*  $\frac{N}{2}$  NaOH solution necessary for this reaction. A comparison of these figures shows how much the *approximately*  $\frac{N}{2}$  NaOH needs diluting to make it *exactly*  $\frac{N}{2}$ .

## SAMPLE CALCULATION

FOR THE DETERMINATION OF THE ABSOLUTE VALUE  
AND THE  
DETERMINATION OF THE QUANTITIES TO BE ADDED TO MAKE  
AN EXACTLY  $\frac{N}{2}$  SOLUTION OF NaOH

When standardized with oxalic acid,



Weight of oxalic acid used = 0.7500 gram.

Volume required of approximately  $\frac{N}{2}$  NaOH used in *this* titration, 20 c.c.

$$126.05 : 80.02 = 0.7500 : x$$

$$x = 0.4761 \text{ gram NaOH.}$$

Therefore 0.7500 gram  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$  requires 0.4761 gram NaOH. Therefore 20 c.c. of this solution contain 0.4761 gram NaOH, and 1 c.c. of this solution contains 0.0238 gram NaOH or this solution contains 23.8 grams NaOH per liter.

If the solution were exactly half-normal, it would contain 20.004 grams NaOH per liter or .020 gram in 1 c.c.

It is therefore too strong and should have added to it 76.9 c.c. of water according to the following:

Should there remain 405 c.c. of the solution, let  $x$  equal the volume required to make the solution exactly  $\frac{N}{2}$ .

Then  $405 \times 0.238 = x \times 0.020.$

$$x = 481.9 \text{ c.c.}$$

$$481.9 \text{ c.c.} - 405 \text{ c.c.} = 76.9 \text{ c.c., the volume to be added.}$$

(8) *The Reestablishment of the Relative Values of the two Solutions*

If time permits, the correctness of the preceding work may be verified by the reestablishment of the relative values of the two adjusted solutions, equal volumes of which should now neutralize each other.

PROCEDURE

Take an accurately measured volume of from 10 to 20 c.c. of either solution.

Use *methyl orange* as an indicator.

Determine the volume of the other solution necessary to effect neutralization.

**THE VOLUMETRIC DETERMINATION  
OF THE  
TOTAL ALKALI IN SODA ASH<sup>95</sup>**

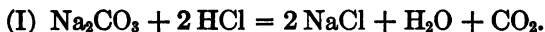
*A Typical Saturation Process*

This method is applicable to the titration of caustic soda, caustic potash, or alkali carbonates.

Soda ash,  $\text{Na}_2\text{CO}_3$ , etc., is:

- (a) dried to determine the moisture;
- (b) neutralized with standard hydrochloric acid;
- (c) calculated as "total available alkali."

**TYPE REACTIONS**



---

**EXPLANATORY FACT**

95. Soda ash is calcined crude sodium carbonate resulting from either the "Le Blanc" or the "Ammonia" process for making soda. It contains a little sodium hydroxid, often traces of sulfids, thiosulfates, sulfites, sulfates, silicates and chlorids. There also may be present alumina and ferric oxid. "Le Blanc" soda has, as its chief impurity, sodium sulfate, while "Ammonia" soda is generally free from caustic soda, ( $\text{NaOH}$ ), sulfid and sulfate, and contains the most chlorid. "Ammonia" soda (0.8) is lighter than "Le Blanc" soda (sp. g. 1.2).



PROCEDURE <sup>96</sup>

Weigh an ignited platinum crucible.

Weigh about 5 grams <sup>97</sup> of the sample into the crucible.

Heat to dull redness for about twenty minutes.<sup>98</sup>

Cool in a desiccator.

Expelling the moisture from the soda ash

Weigh and repeat the heating for a few minutes until a constant weight is reached.

Calculate the loss in weight as moisture.

Transfer the contents of the crucible to a 500 c.c. (No. 4) beaker.

Wash the crucible thoroughly and catch the washings in the beaker.

Preparation of the solution of the soda ash

Add about 100 c.c. of water and stir.

Warm, if necessary, till all is dissolved that will dissolve.

Transfer this solution quantitatively through a filter directly into a 250 c.c. volumetric flask.

Filtration of the solution

Wash the filter paper and insoluble residue with a stream of hot water from a water bottle till a drop of the filtrate gives no further reaction with litmus paper.

---

EXPLANATORY FACTS

96. In the analysis of soda ash, German alkali manufacturers (1) always ignite the soda ash before determining the per cent. of alkali and calculate the results on the ignited material and (2) they include in the total per cent. of alkalinity, that which is due to the insoluble portion, calcium and magnesium carbonates, ferric oxid, etc., as well as the soluble portion. Since the total insoluble matter (including nonalkaline substances like sand) is very small, there is but slight difference in the percent. of alkalinity in the soda ash whether analyzed by the German or other methods.

97. In the above determination, an unignited sample is weighed and the soluble alkali only is determined.

98. If this temperature is exceeded, the mass will fuse.

Cool to the "graduation temperature"<sup>99</sup> of the flask and add water up to the graduation line. Some of this water that is added should be directed down all parts of the inside of the neck of the flask to make sure that all of the solution is collected in its bulb.

Dry the inner neck down to the liquid level, using a filter paper rolled around a glass rod.

Mix the liquid thoroughly by pouring it back and forth from the flask into a dry beaker.<sup>100</sup>

After this keep the flask stoppered.

Preparation of  
aliquot parts

Titration is to be made with aliquot parts of 50 c.c. each of this solution. This amount may be measured in pipets or volumetric flasks of this capacity.

Rinse twice the selected measuring instrument with a little of the solution before the aliquot part is measured.<sup>101</sup>

Pour the measured 50 c.c. into a clean 250 c.c. flask.

Wash out the graduated flask quantitatively into the titrating flask.

Dilute the 50 c.c. to about 100 c.c.

---

#### EXPLANATORY FACTS

99. The graduation temperature is usually marked on graduated measuring apparatus. It is about room temperature, that is, 60° F., or 17.5° C., a temperature decided upon by Mohr. A true liter is the volume of one thousand grams of water at 4° C. As a more practical unit one thousand grams of water at 17.5° C. is taken and is called the "Mohr Liter."

100. Since the solution has now been mixed sufficiently to make it homogeneous and since only aliquot parts of it are to be used for titration neither that adhering to the beaker nor that which is to be used for rinsing the pipet or 50 c.c. flask need be considered.

101. Of course the amount of soda ash in each aliquot part corresponds to one-fifth of the original weight taken.

Add three or four drops of *methyl orange* solution.<sup>102</sup>

From the buret, after noting the reading, add a slight excess of

$\frac{N}{2}$  HCl.

Note the reading and titrate back with  $\frac{N}{2}$  NaOH and find

the point at which a drop of either solution changes the color from yellow to pinkish red or *vice versa*. Titration of the  
alkaline solution

End the titration with the acid.

Take readings for both acid and alkali.

Repeat this determination with another 50 c.c. of the soda ash solution.

---

#### EXPLANATORY FACT

102. Methyl orange is unaffected by the CO<sub>2</sub> that is liberated when the acid is added to the carbonate. Most indicators show an acid reaction with the CO<sub>2</sub> which makes the alkali solution appear to be neutralized before such is the case. With such indicators the solution must be kept at the boiling point to drive off the CO<sub>2</sub>.

## SAMPLE CALCULATION

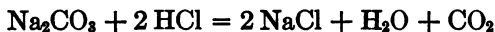
Weight of soda ash taken = 4.9706.

Solution made up to 250 c.c.; one-fifth of this, 50 c.c., titrated.  
 $4.9706 \div 5 = 0.9941$  gram weight of soda ash in each 50 c.c.

What is the weight of the gaseous HCl in 1 c.c. of exactly  $\frac{N}{2}$  HCl?

$$\frac{\text{HCl (36.46)}}{2} \div 1000 = 0.01823 \text{ gram.}$$

How much  $\text{Na}_2\text{CO}_3$  is equivalent to 1 c.c. of exactly  $\frac{N}{2}$  HCl?



$$106 : 72.92 = x : 0.01823$$

$$x = 0.0265 \text{ gram,}$$

or 0.0265 gram of  $\text{Na}_2\text{CO}_3$  is equivalent to 1 c.c. of  $\frac{N}{2}$  HCl.

## TITRATIONS

$$\begin{array}{rcl} \frac{N}{2} \text{HCl} & & \frac{N}{2} \text{NaOH} \\ 39.92 \text{ c.c.} & & 2.82 \text{ c.c.} \\ 1 \text{ c.c. of } \frac{N}{2} \text{HCl} = 1 \text{ c.c. of } \frac{N}{2} \text{NaOH} \end{array}$$

$39.92 - 2.82 = 37.10$  c.c. of  $\frac{N}{2}$  HCl actually used to neutralize the soda ash.

$37.10 \frac{N}{2}$  HCl is equivalent to

$$37.10 \times 0.0265 = 0.98315 \text{ gram of } \text{Na}_2\text{CO}_3.$$

What per cent. is 0.98315 of 0.9941?

$$\frac{0.98315}{0.9941} = \underline{\underline{98.89}} \text{ per cent total alkali.}$$

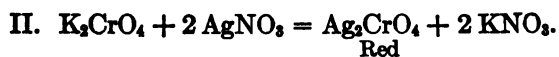
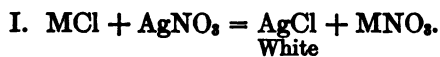
THE VOLUMETRIC DETERMINATION OF CHLORIN  
IN AN  
UNKNOWN SALT

*A Typical Precipitation Process*

The salt is:

- (a) dissolved in water;
- (b) titrated with approximately  $\frac{N}{10}$   $\text{AgNO}_3$  with potassium chromate as an indicator;
- (c) calculated as per cent. of chlorin.

REACTIONS



## THE DETERMINATION OF CHLORIN

## PROCEDURE

Weigh into a six-inch evaporating dish or, if the titration is to be done on a white surface, into a 350 c.c. beaker if preferred, two portions of the unknown salt Weighing the charge of about 0.3 gram each.

Receive from the instructor about 250 c.c. of approximately  $\frac{N}{10}$  *silver nitrate solution*  $\left(\frac{169.89 \text{ grams}}{10}\right)$  which must be poured into a perfectly clean but not necessarily dry bottle. This solution must be kept closely stoppered and as much away from the light as possible.

STANDARDIZATION OF THE APPROXIMATELY  $\frac{N}{10}$  SOLUTION OF  
SILVER NITRATE TO DETERMINE ITS STRENGTH IN  
TERMS OF CHLORIN

Weigh about 0.3 gram of pure fused *sodium chlorid* (as a standard). Weighing the  
standard salt

Dissolve in cold water.<sup>103</sup>

Titrate with the approximately  $\frac{N}{10}$  *silver nitrate solution* using as  
an indicator *potassium chromate* free from  
chlorin.<sup>104</sup> \* Titration for stand-  
ardization of the  
solution

Calculate

- (1) the value of 1 c.c. of the  $\text{AgNO}_3$  in terms of  $\text{NaCl}$ ,
- (2) the per cent. of  $\text{Cl}$  in  $\text{NaCl}$  and
- (3) the value of 1 c.c. of this solution of  $\text{AgNO}_3$  in terms of chlorin.

In an exactly  $\frac{N}{10}$  solution of  $\text{AgNO}_3$ , 1 c.c. corresponds to 0.003545 gram of  $\text{Cl}$ .

#### EXPLANATORY FACTS

103. The solution of the salt must be practically neutral, as acids exercise a solvent action on  $\text{Ag}_2\text{CrO}_4$ . If present, acids must be neutralized with "chlorin-free" sodium carbonate. An excess of alkali, however, is to be avoided, as it will cause a precipitation of  $\text{Ag}_2\text{CO}_3$ .

104. As long as any chlorin remains unprecipitated, no red color forms. The permanent formation of the red  $\text{Ag}_2\text{CrO}_4$  indicates the end point.

\* "Chemistry of the Metals," Experiments Nos. 51 and 54.

## PROCEDURE

Titrate the unknown salt just as the pure sodium chlorid was titrated, using  $K_2CrO_4$  as an indicator.

Titration of the  
unknown salt



## SAMPLE CALCULATIONS

*Standardization of AgNO<sub>3</sub> Solution*

1. Weight of pure NaCl taken = 0.2603 gram.

Approximately  $\frac{N}{10}$  AgNO<sub>3</sub> used = 44.70 c.c.

$$\frac{0.2603}{44.70} = 0.005823;$$

that is, 1 c.c. of the AgNO<sub>3</sub> solution = 0.005823 gram of NaCl.

2. The per cent. of chlorin in NaCl = 60.65.

(The student is to show by calculation in the notebook that this is so.)

3. 60.65 per cent. of 0.005823 = 0.003532.

Therefore, 1 c.c. of AgNO<sub>3</sub> = 0.003532 gram of Cl.

## DETERMINATION

Weight of unknown salt used = 0.3064 grams.

Volume of AgNO<sub>3</sub> used = 42.60 c.c.

$$\frac{0.003532 \times 42.60}{0.3064} = \underline{\underline{49.10}} \text{ per cent. chlorin.}$$

## THE VOLUMETRIC DETERMINATION OF IRON IN AN ORE

Iron is:

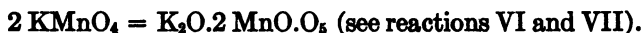
- (a) converted to ferric chlorid,  $\text{FeCl}_3$ , by dissolving the ore in hydrochloric acid;
- (b) changed to ferric sulfate,  $\text{Fe}_2(\text{SO}_4)_3$ , by evaporation with concentrated sulfuric acid;
- (c) reduced to ferrous sulfate,  $\text{FeSO}_4$ , by zinc and by hydrogen;
- (d) titrated with  $\frac{N}{10}$  potassium permanganate,  $\text{KMnO}_4$ ;
- (e) calculated as per cent. of iron.

### REACTIONS

- I.  $\text{Fe}_2\text{O}_3 + 6 \text{HCl} = 2 \text{FeCl}_3 + 3 \text{H}_2\text{O}.$
- II.  $2 \text{FeCl}_3 + 3 \text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + 6 \text{HCl}.$
- III.  $\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2.$
- IV.  $\text{Fe}_2(\text{SO}_4)_3 + \text{Zn} = \text{ZnSO}_4 + 2 \text{FeSO}_4.$
- V.  $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2 = 2 \text{FeSO}_4 + \text{H}_2\text{SO}_4.$
- VI.  $10 \text{FeSO}_4 + 2 \text{KMnO}_4 + 8 \text{H}_2\text{SO}_4$   
 $\quad = 5 \text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 2 \text{MnSO}_4 + 8 \text{H}_2\text{O}.$
- VII.  $10 \text{FeO} + 50 = 5 \text{Fe}_2\text{O}_3.$

PREPARATION OF AN  $\frac{N}{10}$  SOLUTION OF POTASSIUM PERMANGANATE,  $\text{KMnO}_4$  (158.03)

As an oxidizing agent in acid solution, potassium permanganate splits up as follows:



Each *two* molecules of  $\text{KMnO}_4$  furnish five available oxygen atoms, which are equivalent to ten hydrogen atoms. *One* molecule of  $\text{KMnO}_4$  therefore is equivalent to five atoms of hydrogen.

The molecular weight of  $\text{KMnO}_4 = 158.03$ .

This expressed in grams = 158.03 grams.

A normal solution of potassium permanganate used as an oxidizing agent contains in one liter 31.60 grams, one-fifth of its molecular weight in grams. A decinormal solution contains  $\frac{31.60}{10}$  or 3.16 grams in one liter.

#### PROCEDURE

Prepare half a liter of an  $\frac{N}{10}$  solution of *potassium permanganate*. Making the standard solution

Warm slightly to aid solution.

Filter through asbestos on a Witt plate.

### STANDARDIZATION OF THE $\frac{N}{10}$ $\text{KMnO}_4$ SOLUTION <sup>105</sup>

Rather than make an exact  $\frac{N}{10}$   $\text{KMnO}_4$  solution, it is usual to standardize it in terms of iron or, if it is more convenient, in terms of any other appropriate substance.

Use either iron wire or Mohr's salt,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ . If iron wire is used, it must be free from rust and be of a known percentage purity. If Mohr's salt is used, it must be in clear crystals (those that have lost no water of crystallization) or those from a sample, the iron content of which has been gravimetrically determined.

Method of standardization of the permanganate solution

#### PROCEDURE

Weigh into two Erlenmeyer flasks two samples of *iron wire* of about 0.25 gram each.

Pour into each flask 100 c.c. of dilute *sulfuric acid* (1.5).

Loosely cover each flask with a one-inch watch glass and warm gently till all the iron is dissolved, but do not boil. A few flakes of carbon, which can easily be distinguished as such, will remain.

Standardization of the solution

---

#### EXPLANATORY FACT

105. Solutions of  $\text{KMnO}_4$  undergo decomposition in the light. If they are to be preserved they must be kept either in colored glass bottles or in bottles covered with black paper. Even then, frequent standardization is desirable.

After the foregoing, to be certain that all the iron is in the ferrous state, proceed as follows: Get ready two glass tubes, bent at an angle of about  $45^\circ$ , with the longer limb about twelve inches and the shorter about three inches long. Insert the short limb into a one-hole rubber stopper of proper size for the neck of the flask. Support the two flasks with clamps on ring stands, inclining them at an angle of  $45^\circ$ . When the short limb is inserted into the neck of the flask, the long limb of the glass tube should be vertical.

Reduction of any  
oxidized iron to the  
ferrous state

Put into each flask a very small amount of *solid sodium carbonate*,<sup>106</sup>  $\text{Na}_2\text{CO}_3$ .

Immediately add to each flask a very small amount of "40-mesh," chemically pure granular zinc,<sup>107</sup> and stopper the flask at once.\*

Dip the long end of the tubes into solutions of sodium carbonate contained in small beakers.<sup>108</sup>

Cooling the solution  
in a nonoxidizing  
atmosphere

Gently warm, but do not boil, the solution in the inclined flask till the zinc is dissolved.<sup>109</sup>

---

#### EXPLANATORY FACTS

106. The carbon dioxide thus evolved will expel air from the flasks.

107. The introduction of the zinc will cause the reduction to the ferrous state of any iron which might possibly have been oxidized during solution (see reactions IV and V). The presence of zinc sulfate in the solution (see reaction III) does not affect the titration with potassium permanganate.

108. Although the hydrogen can escape, yet, since the end of the long tube is sealed by the sodium carbonate solution, any ingress of air is impossible.

109. As the zinc dissolves, the inclined position of the flask prevents loss by spattering.

\* "Chemistry of the Metals," Experiment No. 156.

Allow the flask to become cold.<sup>110</sup>

As soon as the solution is quite cold, it should be at once titrated to a faint pink color with the *potassium permanganate* solution.<sup>111&112</sup>

Titration of the  
ferrous sulfate

---

### EXPLANATORY FACTS

110. As the solution in the flask cools, the sodium carbonate solution in the beaker rises in the tube, but the first drop coming into the flask causes effervescence and the liquid is driven back down the tube. This gradual equalization of pressure continues until equilibrium is established.

111. All solutions titrated with permanganate of potassium must be acid—preferably with sulfuric acid—in order to keep the manganous oxid in solution.

112. It is often convenient to have on hand a solution of Mohr's salt a sample of which has been titrated with the  $\text{KMnO}_4$  solution so that the value of one cubic centimeter of the Mohr's salt solution in terms of the permanganate solution may have been previously established. If the end point should ever be exceeded, the solution may then be "titrated back" with the Mohr's salt solution and allowance made for the  $\text{KMnO}_4$  which by mistake was added in excess.

## SAMPLE CALCULATION

Weight of iron = 0.2500 gram (99.85 per cent. pure).

$\frac{N}{10}$   $\text{KMnO}_4$  solution used = 31.18 c.c.

$$\frac{0.2500 \times 0.9985}{31.18} = 0.0080. \quad \text{That is,}$$

1 c.c. of the  $\text{KMnO}_4$  solution is equivalent to 0.0080 gram of iron.

**DETERMINATION OF THE IRON***Preparation of the Ore for Analysis*

It is impossible to dissolve and therefore to analyze an ore of this nature that has not been ground to an impalpable powder too smooth to grit between the teeth. This is often a long and tedious operation and should have been begun before the student has reached this determination (see page 122). Mortars cut from agate (a form of quartz) must be used. Do not put much more of the ore in the mortar at one time than can be held on the tip of a small spatula. When ground to an impalpable powder, transfer to a weighing tube and grind other portions until at least a gram of the ore is ready.

**PROCEDURE**

Weigh out into porcelain crucibles two portions of the ground ore of about 0.5 gram each.

Heat these crucibles in the Bunsen flame for about ten minutes.<sup>113</sup>

Roasting the ore

---

**EXPLANATORY FACT**

113. Iron ores often contain organic matter, which, as it might be later acted upon by the permanganate and vitiate the results, must be destroyed by "roasting." Moreover, it also colors the insoluble residue and makes it difficult to tell when the solution of the ore is complete.



Cool the crucibles and transfer their contents to two 250 c.c. casseroles. If all the ore cannot be removed, the crucibles themselves must be put into the casseroles as well.<sup>114</sup>

Add to each sample 25 c.c. of *hydrochloric acid* (1.2 sp. gr.).

Cover the casseroles and let the ore digest at a temperature just below boiling<sup>115</sup> for from thirty minutes to an hour. This will generally effect complete decomposition as shown by a white residue. If after this time the solvent action appears to have ceased and the residue is still dark, proceed as follows:

Preparation of the  
solution

Dilute the solution, filter off and wash the residue till the washings give no test for acid.

Ignite the filter paper and residue in a platinum crucible and fuse<sup>116</sup> the ash with a small quantity of *sodium carbonate*,  $\text{Na}_2\text{CO}_3$ .

Fusion of any  
insoluble residue

After cooling, partly fill the crucible with water and cautiously boil.

---

### EXPLANATORY FACTS

114. *Platinum* crucibles must not be put into iron solutions.

115. The iron oxid in most iron ores, if ground to an impalpable powder, is wholly soluble in strong hydrochloric acid. Hard or prolonged boiling or too great concentration of the solution of  $\text{FeCl}_3$  must be avoided to prevent loss of iron. In the laboratories of some steel works, it is customary to leave the ore in the hydrochloric acid on steam baths over night. The next day the solution is usually complete. Some analysts advocate adding a few drops of nitric acid to hasten the solution.

116. By fusion, the insoluble substances are transformed into such compounds as silicates of the alkalis, carbonates of the heavy metals, etc. This fused mass is entirely decomposed by treatment with dilute hydrochloric acid. Therefore, any iron which may have remained undissolved by the original treatment with acid is now obtained in the solution as  $\text{FeCl}_3$ .

Add this solution and any residue to the original hydrochloric acid solution.

Carefully wash out the platinum crucible and add the washings to the solution. Solution of the fusion

Warm until effervescence ceases.

Whether or not this secondary process was needed, a *white* residue need not be filtered off.

Add about 5 c.c. of *concentrated sulfuric acid* to the cooled hydrochloric acid solution. Conversion to the sulfate

Evaporate under the hood until fumes of  $\text{SO}_3$  are evolved.<sup>117</sup>

Cool the solution and dilute to about 100 c.c.

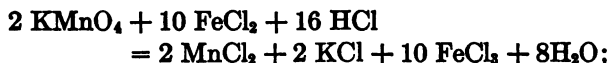
Warm the liquid until nothing but flocculent silica remains undissolved.

Transfer quantitatively to a 250 c.c. flask.

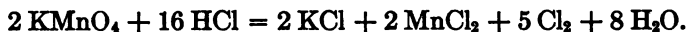
Add 5 grams of "40-mesh" C. P. *granular zinc* and put rubber stoppers carrying the bent glass tubes, as described on page 147, into the flasks. Reduction of the iron The tubes should, as before, dip into the sodium carbonate solution. *Avoid hydrogen explosions!*

#### EXPLANATORY FACT

117. Potassium permanganate in the presence of hydrochloric acid causes the oxidation of ferrous salts, as will be seen by the following:



but it is also true that



The titration with permanganate, then, in the presence of hydrochloric acid, is attended with a possibility of loss unless special precaution, such as adding  $\text{MnSO}_4$ , etc., is taken. It is therefore customary to remove all the hydrochloric acid by means of this evaporation with sulfuric acid (see reaction II).

Allow the zinc to dissolve *entirely*. Aid the process at the last by a gentle heat. *Do not boil.*

With the tubes still sealed by the sodium carbonate solution, allow the solutions to cool. The action will be the same as described on page 148.

Cooling the  
solution

When cool,<sup>118</sup> the solution should be at once titrated with the standardized permanganate solution.

Titration of the  
iron

---

#### EXPLANATORY FACT

118. The complete reduction may be tested for as follows: Withdraw a minute drop of the solution on the end of a "drawn out" glass rod and touch it to a drop of KSCN solution on the white tile of the buret stand. If no red color forms, the reduction is complete. If a red color does appear, more zinc must be added and the process repeated.

## SAMPLE CALCULATION

Weight of ore used = 0.5603 gram.

KMnO<sub>4</sub> solution used = 32.68 c.c.

Standardization of KMnO<sub>4</sub> solution is 0.0080 of gram of iron (see page 149).

$32.68 \times 0.0080 = 0.2614$  gram of iron in 0.5306 gram of ore.

$$\frac{0.2614}{0.5306} = \underline{\underline{49.26}} \text{ per cent. of iron.}$$

**FACTORS NEEDED FOR THE DETERMINATIONS IN GRAVIMETRIC  
WORK INCLUDED IN THIS BOOK\***

Determina- tion of	Weighed as,	Required.	Factor.	Log.
Al	$\text{Al}_2\text{O}_3$	Al	0.53033	$\bar{1}.72455$
Cu	CuO	Cu	0.79891	$\bar{1}.90250$
Fe	$\text{Fe}_2\text{O}_3$	Fe	0.69944	$\bar{1}.84475$
$\text{SO}_4$	$\text{BaSO}_4$	$\text{SO}_4$	0.41155	$\bar{1}.61442$
Cl	AgCl	Cl	0.24738	$\bar{1}.39337$
MgO	$\text{Mg}_2\text{P}_2\text{O}_7$	MgO	0.36219	$\bar{1}.55894$

\* Other factors, if needed, may be found in Olsen's Chemical Annual, in the "Chemiker Kalender," or Treadwell's Quantitative Analysis.

## INTERNATIONAL ATOMIC WEIGHTS

0=16		0=16	
Aluminum	Al 27.1	Molybdenum	Mo 96.0
Antimony	Sb 120.2	Neodymium	Nd 144.3
Argon	A 39.9	Neon	Ne 20.0
Arsenic	As 75.0	Nickel	Ni 58.68
Barium	Ba 137.37	Nitrogen	N 14.01
Bismuth	Bi 208.0	Osmium	Os 190.9
Boron	B 11.0	Oxygen	O 16.00
Bromin	Br 79.92	Palladium	Pd 106.6
Cadmium	Cd 112.40	Phosphorus	P 31.0
Cæsium	Cs 132.81	Platinum	Pt 195.0
Calcium	Ca 40.07	Potassium	K 39.1
Carbon	C 12.00	Praseodymium	Pr 140.6
Cerium	Ce 140.25	Radium	Ra 226.4
Chlorin	Cl 35.46	Rhodium	Rh 102.9
Chromium	Cr 52.1	Rubidium	Rb 85.45
Cobalt	Co 58.97	Ruthenium	Ru 101.7
Columbium	Cb 93.5	Samarium	Sa 150.4
Copper	Cu 63.57	Scandium	Sc 44.1
Dysprosium	Dy 162.5	Selenium	Se 79.2
Erbium	Er 167.7	Silicon	Si 28.3
Europium	Eu 152.0	Silver	Ag 107.88
Fluorin	F 19.0	Sodium	Na 23.00
Gadolinium	Gd 157.3	Strontium	Sr 87.62
Gallium	Ga 69.9	Sulphur	S 32.07
Germanium	Ge 72.5	Tantalum	Ta 181.5
Glucinum	Gl 9.1	Tellurium	Te 127.5
Gold	Au 197.2	Terbium	Tb 159.2
Helium	He 4.0	Thallium	Tl 204.0
Hydrogen	H 1.008	Thorium	Th 232.42
Indium	In 114.8	Thulium	Tm 168.5
Iodin	I 126.92	Tin	Sn 119.0
Iridium	Ir 193.1	Titanium	Ti 48.1
Iron	Fe 55.84	Tungsten	W 184.0
Krypton	Kr 82.9	Uranium	U 238.5
Lanthanum	La 139.0	Vanadium	V 51.06
Lead	Pb 207.1	Xenon	Xe 128.0
Lithium	Li 7.0	Ytterbium (Neoytter- bium)	Yb 172.0
Lutecium	Lu 174.0	Yttrium	Y 89.0
Magnesium	Mg 24.32	Zinc	Zn 65.37
Manganese	Mn 54.93	Zirconium	Zr 90.6
Mercury	Hg 200.6		

## LOGARITHMS

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.									
											1	2	3	4	5	6	7	8	9	
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37	
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34	
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31	
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29	
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27	
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25	
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24	
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22	
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21	
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20	
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19	
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18	
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17	
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17	
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16	
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15	
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15	
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14	
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14	
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13	
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13	
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12	
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12	
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12	
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11	
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11	
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11	
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10	
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10	
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10	
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10	
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9	
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9	
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9	
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9	
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9	
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8	
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8	
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8	
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8	
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	4	5	6	6	7

## LOGARITHMS—Continued

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	6	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	6	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	6
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	6
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	6
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	6
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4



## LOGARITHMS. — Continued

Logarithms.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	2	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	2	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	2	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	2	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	2	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	2	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	2	2	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	2	2	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	1	2	2	2	2	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	1	2	2	2	2	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	1	2	2	2	2	3
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	1	2	2	2	2	3
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	1	2	2	2	2	3
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	1	2	2	2	2	3
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	1	2	2	2	2	3
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	1	2	2	2	2	3
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	1	2	2	2	2	3
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	1	2	2	2	2	3
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	1	2	2	2	2	3
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	1	2	2	2	2	3
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	1	2	2	2	2	3
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	2	2	2	2	3
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	2	2	2	2	3
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	2	2	2	2	3
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	2	2	2	2	3
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	2	2	2	2	3
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	2	2	2	2	3
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	2	2	2	2	3
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	2	2	2	2	3
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	2	2	2	2	3
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	2	2	2	2	2	3
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	2	2	2	2	2	3
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	2	2	2	2	2	3
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	2	2	2	2	2	3
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	2	2	2	2	2	3
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	2	2	2	2	2	3
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	2	2	2	2	2	3

## LOGARITHMS—Concluded

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	6	7	8
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	6	7	8
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	7	8
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	7	8
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	3	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	3	4	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9944	9977	2	5	7	9	11	14	16	18	20

## INDEX

---

	PAGE
Absolute value of a standard hydrochloric acid solution, determination of .	121
Acidimetry . . . . .	112
Aliquot part . . . . .	90, 136
Alkalimetry . . . . .	112
Alkalinity, total, of soda ash, determination of . . . . .	134
Alloy for electrolytic determination . . . . .	89
Aluminium, determination of, in alum . . . . .	33
removal of, from dolomite . . . . .	71
Analysis, gravimetric and volumetric, compared . . . . .	2, 97
Anode . . . . .	86
Apparatus . . . . .	5
for measuring volume of liquids . . . . .	98
 Balances . . . . .	 10
adjustment of . . . . .	11
Barium sulfate, precipitating and filtering of . . . . .	59
Baths, air and steam . . . . .	7
Burets . . . . .	99
reading of . . . . .	100
 Calcium, determination of, in a mineral . . . . .	 73
Calcium oxalate, purification of . . . . .	74
Calculation . . . . .	27
Calibration of apparatus for measuring volume . . . . .	98
Cathode and cation . . . . .	86
Checking of weights by instructor . . . . .	16, 30
Chlorin, gravimetric determination of, in a soluble salt . . . . .	62
volumetric determination of, in a soluble salt . . . . .	139

	PAGE
Cleaning volumetric glassware.....	101
Constant weight.....	28
Coolers for reduced iron solutions.....	147
Copper in an alloy, electrolytic determination of.....	92
determination of, in copper sulfate.....	45
sulfate, preparation of pure crystals of.....	46
oxid, method of igniting.....	49
Crucibles.....	7
cleaning of.....	8
Gooch.....	25
Current density.....	86
Decantation.....	23
Desiccators.....	10
use of.....	41
Dissociation.....	20, 85
Dolomite (or similar minerals), analysis of.....	68
Electrodes.....	86
drying of.....	92
Electrolysis.....	86
Electrolyte.....	86
Electrolytic Analysis.....	85-94
Electrolytic determinations.....	87
End point, determination of.....	103
Evaporations.....	7, 24
Factors, calculation and use of.....	27, 155
for approximately normal solutions.....	119
Filter flasks.....	7
Filtering.....	22
Filter paper.....	5, 22
for barium sulfate.....	60
tared.....	25
Filtration, arrangement of apparatus for.....	36
Funnels.....	6
Fusion of insoluble substances.....	17, 79
Gibbs, Wolcott, method of, for magnesium.....	76
Glassware, cleaning of surface of, in volumetric analysis.....	101
Gooch crucibles.....	25
Gravimetric Analysis.....	33-81
definition of.....	12

# INDEX

163

	PAGE
Hydrochloric acid, preparation of half-normal solution of.....	113
determination of absolute value of solution of.....	121
dilution of solution of, to an exact value.....	124, 127
Iceland spar, use of, as a standard.....	122
Ignition of precipitates.....	25
Indicators.....	105
Ions.....	20, 85
Iron, gravimetric determination of, in a soluble salt.....	53
volumetric determination of, in a soluble salt.....	144
and $\text{SO}_4$ , separation of.....	55, 58
removal of, from dolomite.....	71
Isolation of elements or radicals.....	17
Lacmoid.....	107
Liquid level, reading of.....	99, 100
Litmus.....	106
Magnesium, determination of, in dolomite.....	76
Magnesium oxalate, properties of.....	74
Magnesium ammonium phosphate, ignition of, to magnesium pyrophosphate.....	77
Manganese, removal of, from dolomite.....	71
Measuring flasks.....	99
Meniscus.....	99, 100
Methyl orange.....	106
Microcosmic salt, use of, for the determination of magnesium.....	76
Normal solutions.....	108
adjustment of, by dilution to an exact volume....	124, 127, 128, 132
Notebooks.....	30
Permanency of standard solutions.....	111
Phenolphthalein.....	107
Pipets.....	98
Platinum, rules for use of.....	8
"Policeman," use of, for removing precipitates.....	5, 38
Potassium cyanid, use of.....	89, 90
Potassium permanganate, preparation and standardization of a tenth-normal solution of.....	145

	PAGE
Precipitates, drying of.....	7, 39, 40
ignition of.....	25, 40
purification of.....	18
washing of.....	17, 20
Precipitation.....	17, 20
Qualitative and quantitative analysis, comparison of.....	1
Quills, use of, for removing precipitates.....	38
Radical $\text{SO}_4$ , gravimetric determination of, in a soluble salt.....	57
Reagents.....	17
amounts of, to add.....	18
Records, types of.....	31, 43
Relative values of acid and alkali solutions, determination of.....	116
Separation of elements or radicals.....	17
Silica, determination of, in minerals and rocks.....	78
purification of, by hydrofluoric acid.....	81
removal of, from dolomite.....	70
from iron ore.....	151
Silicates, fusion of, to accomplish solution.....	17, 79
Silicic acid, dehydration of.....	70, 80
Silver, electrolytic determination of.....	91
Silver chlorid, action of light upon.....	63, 66
method of igniting.....	65
Silver nitrate, standardization of a solution of.....	141, 143
Soda ash, determination of total alkalinity of.....	134
Sodium hydroxid, dilution of a solution of, to exact value....	128, 131, 132
preparation of a half-normal solution of.....	115
standardization of, against oxalic acid.....	129
Solubilities, table of.....	21
Solution, process of.....	17
Solutions, facts regarding.....	19
homogeneity of.....	19
Solvents.....	19
Standard solutions.....	102
permanency of.....	111, 115
dilution of, to exact value.....	121, 125
Study outside the laboratory.....	32
Suction for filtrations.....	7, 22
Sulfuric acid, determination of, in a soluble salt.....	57
Tared filter papers.....	25
Titration.....	102

## INDEX

165

	PAGE
Volumetric Analysis.....	97-154
definition of.....	97
Washing of precipitates.....	22, 37, 38
test for the completion of.....	22
Washing by decantation.....	23, 37
Weighing, directions for.....	15
precautions for.....	13
Weighing tubes.....	6
Weights, analytical.....	11
average approximate.....	15
constant.....	26
Work, planning of.....	29
Zero point, determination of.....	14
Zinc, "40-mesh," use of, to reduce iron in volumetric determination...	147

UNIV. OF

SEP 26 1913





**T**HE following pages contain advertisements of a few of the Macmillan books on kindred subjects.



# Qualitative Chemical Analysis

WITH EXPLANATORY NOTES

By ARTHUR A. NOYES, Ph.D.

*Assistant Professor of Chemistry in the Massachusetts Institute of Technology.*

"Having used the principal methods embodied in this work for more than twenty years, I can assert that they will give satisfactory results in teaching qualitative analysis with large as well as with small classes. The arrangement is excellent."—Professor C. F. MABERY, *Case School of Applied Science*.

"This book we have used here for two years and shall continue to do so indefinitely; since it was eminently satisfactory before and is more so in its revised form."—HERBERT R. MORLEY, *Gilbert School, Winsted, Conn.*

"I have used this work to some extent, and as a practical treatise on analytical chemistry find it to excel in just those points where other books of its kind usually fail; viz. in indicating precise methods of procedure as well as giving the rationale of the process employed."—Dr. W. H. HIGBEE, *Hamilton College*.

"It is the sort of manual I have been looking for, for use in my class, and I expect to give it a trial next year."—Professor W. P. BRADLEY, *Wesleyan University*.

"It is plain, accurate, sensible—written evidently by a sensible man and careful teacher."—Professor F. C. ROBINSON, *Bowdoin College*.

"I regard it as a most excellent book."—Professor EDGAR F. SMITH, *University of Pennsylvania*.

*Cloth, 8vo, \$1.25 net.*

# Qualitative Chemical Analysis

WITH EXPLANATORY NOTES AND STOICHIOMETRICAL PROBLEMS

By HENRY P. TALBOT, Ph.D.

*Associate Professor of Analytical Chemistry in the Massachusetts Institute of Technology.*

"It is a most excellent and needed addition to our help in teaching Quantitative Analysis. I have recommended it to my class in the subject."—Professor A. W. SMITH, *Case School of Applied Science*.

"This book is written directly from an experienced teacher's standpoint, and it attains its end quickly and intelligently. In many laboratories the student cannot always have the continuous advice and aid of an assistant. The student must, under such circumstances, learn to think more independently. That his thoughts may be properly guided, after a general discussion of, and following each method given for analysis, are numbered paragraphs giving the reactions occurring, with reasons and necessary precautions for obtaining successful results. The neatly bound, well printed book deserves high commendation."—Professor C. BASKERVILLE, *University of North Carolina*.

"It is an excellent work, carefully prepared, and on a plan that will supply a want in teaching quantitative analysis."—Professor C. F. MABERY, *Case School of Applied Science*.

"We find in Professor Talbot's Introductory Course of Chemical Quantitative Analysis something more than a book for local use. There is an idea running through it that is more or less new in books of this kind, and one which instructors will heartily welcome. There is an attempt to give the student not only the important and essential things which he should know in special cases, but what is of more importance, so to direct his thoughts toward his work that he shall grasp the fundamental ideas governing chemical analysis. In other words, the directions and explanations are such as the thoughtful and conscientious teacher would give to his pupil in the laboratory in endeavoring to make him think for himself intelligently."—T. M. DROWN, *President Lehigh University, in the Journal of the American Chemical Society*.

*Cloth, 8vo, \$1.50 net.*

PUBLISHED BY

THE MACMILLAN COMPANY

64-66 Fifth Avenue, New York

# A LIST OF WORKS ON CHEMISTRY

*Published by the Macmillan Company*

- KAHLENBERG. Outlines of Chemistry.** A textbook for college students. By LOUIS KAHLENBERG, Ph.D., Professor of Chemistry and Director of the Course in Chemistry in the University of Wisconsin. Published in New York, 1909. *Cloth, 8vo, 548 pages, \$2.60 net.*
- STODDARD. Introduction to General Chemistry.** By JOHN T. STODDARD, Professor of Chemistry at Smith College, Northampton, Mass. New York, 1910. *Now ready.*
- GOOCH & WALKER. Outlines of Inorganic Chemistry.** By FRANK AUSTIN GOOCH, Professor of Chemistry in Yale University, and CLAUDE FREDERIC WALKER, Teacher of Chemistry in the High School of Commerce of New York City. *Cloth, 514 pages, \$1.75 net.*
- JONES. Principles of Inorganic Chemistry.** By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. New York. Third Edition, 1906. *Cloth, 521 pages, \$3.00 net.*
- JONES. Elements of Inorganic Chemistry.** By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. New York, 1903. Second Edition, 1904. Reprinted, 1908. *Cloth, 12mo, 343 pages, \$1.25 net.*
- OSTWALD. The Principles of Inorganic Chemistry.** By WILHELM OSTWALD. Translated with the author's sanction by Alexander Findlay, M.A., Ph.D., D.Sc. London, 1902. Third Edition, 1908. *Cloth, 8vo, 801 pages, \$6.00 net.*
- ROSCOE & HARDEN. An Inorganic Chemistry for Advanced Students.** By Sir HENRY E. ROSCOE, F.R.S., and ARTHUR HARDEN. London. *Cloth, 8vo, \$1.00 net.*
- ROSCOE & SCHORLEMMER. A Treatise on Chemistry.** By Sir H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Vol. I—THE NON-METALLIC ELEMENTS. London, 1877. Third Edition, 1905. *Cloth, 8vo, 931 pages, \$5.00 net.*
- Vol. II—THE METALS. London, 1878. Third Edition, 1897. Fourth Edition, 1907. *Cloth, 8vo, 1,436 pages, \$7.50 net.*
- Vol. III. Preparing.
- ROSCOE. Lessons in Elementary Chemistry, Inorganic and Organic.** By Sir HENRY E. ROSCOE, D.C.L., LL.D., F.R.S. London, 1902. Latest reprint, 1907. *Cloth, 12mo, 523 pages, \$1.25 net.*
- DOBBIN & WALKER. Chemical Theory for Beginners.** By LEONARD DOBBIN, Ph.D., and JAMES WALKER, Ph.D., D.Sc. London, 1892. Fifth Edition, 1906. *Cloth, 16mo, 240 pages, \$.70 net.*

## A LIST OF WORKS ON CHEMISTRY—*Continued*

- RAMSAY.** *Experimental Proofs of Chemical Theory for Beginners.* By WILLIAM RAMSAY, Ph.D., LL.D., Sc.D., F.R.S. London, 1884. Second Edition, 1893. Reprinted, 1900, 1908. *Cloth, 18mo, 143 pages, \$.60 net.*
- LENGFELD.** *Inorganic Chemical Preparations.* By FELIX LENGFELD, Assistant Professor of Inorganic Chemistry in the University of Chicago. New York, 1899. Reprinted, 1905. *Cloth, 12mo, 67 pages, \$.60 net.*
- BENEDICT.** *Chemical Lecture Experiments.* By FRANCIS GANO BENEDICT, Ph.D. New York, 1901. *Cloth, 12mo, 436 pages, \$2.00 net.*
- PERKIN & LEAN.** *Introduction to the Study of Chemistry.* By W. H. PERKIN, Jr., Ph.D., F.R.S., and BEVAN LEAN, D.Sc., B.A. London, 1896. Seventh reprint, 1906. *Cloth, 12mo, 334 pages, \$.75 net.*
- NERNST.** *Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics.* By Prof. WALTER NERNST, Ph.D., of the University of Göttingen. Revised in accordance with the fourth German edition. London, 1895. Second English edition, 1904. *Cloth, 8vo, 771 pages, \$4.50 net.*
- OSTWALD.** *The Scientific Foundations of Analytical Chemistry.* Treated in an elementary manner. By WILHELM OSTWALD. Translated with the author's sanction by George M. Gowan. London, 1895. Third Edition, 1908. *Cloth, 12mo, 247 pages, \$2.00 net.*
- CHESNEAU.** *Theoretical Principles of the Methods of Analytical Chemistry, based upon Chemical Reactions.* By M. G. CHESNEAU, Ingenieur en chef des Mines: Professeur d'analyse minérale à l'école nationale des Mines. Authorized translation by A. T. Lincoln, Ph.D., Assistant Professor of Chemistry, Rensselaer Polytechnic Institute, and D. H. Carnahan, Ph.D., Associate Professor of Romance Languages, University of Illinois. New York, 1910. *Cloth, 8vo, 184 pages, \$.75 net.*
- JONES.** *Practical Inorganic Chemistry for Advanced Students.* By CHAPMAN JONES, F.I.C., F.C.S., etc. London, 1898. Latest reprint, 1906. *Cloth, 12mo, 239 pages, \$.60 net.*
- BASKERVILLE & CURTMAN.** *Qualitative Analysis.* By Professor CHARLES BASKERVILLE, and Dr. L. J. CURTMAN, College of the City of New York. New York, 1910. *In press.*
- NOYES.** *A Detailed Course of Qualitative Chemical Analysis of Inorganic Substances.* With Explanatory Notes by Arthur A. Noyes, Ph.D. New York, 1899. *Cloth, 8vo, 89 pages, \$1.25 net.*
- MORGAN.** *Qualitative Analysis.* As a laboratory basis for the study of general inorganic chemistry. By WILLIAM CONGER MORGAN, Ph.D., Assistant Professor of Chemistry in the University of California. New York, 1906. Reprinted, 1907. *Cloth, 8vo, 351 pages, \$1.90 net.*
- LIVERSIDGE.** *Tables for Qualitative Chemical Analysis.* Arranged for the use of students by A. LIVERSIDGE, M.A., LL.D., F.R.S., Professor of Chemistry in the University of Sydney. London, 1905. Second Edition. *Cloth, 8vo, 126 pages, \$1.50 net.*

13711

25

1890

UNIVERSITY OF MICHIGAN



3 9015 06449 4787

A 593162